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VAPOUR PHASE CHROMATOGRAPHY

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Proceedings of the Symposium sponsored by the Hydrocarbon Research Group of the Institute of Petroleum held at the Institution of Electrical Engineers, London, on 30th May–1st June, 1956

Edited by

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FOREWORD

In the summer of 1955 the Hydrocarbon Research Group of the Institute of Petroleum decided, in view of the rapidly increasing interest in gas chromatography, that the time was opportune to hold a symposium on the subject along the lines of those in 1951 and 1953 on modern spectroscopic methods. The Hydrocarbon Chemistry Panel of the Group formed, for this purpose, a small committee composed of Dr S. F. Birch (Chairman), Mr H. C. Rampton (Secretary and Treasurer), Mr. D. H Desty (Editor), Drs D. Ambrose, R. R. Gordon, A. T. James, and A. J. P. Martin, and Mr G. Sell.

Invitations to submit contributions met with an excellent response and through the cooperation of the authors and publishers it was possible to provide a bound volume of preprints some weeks before the meeting. These contributed in no small measure to the success of the meeting, giving members an opportunity to peruse the papers beforehand and to prepare considered discussion.

The symposium, held in London at the Institution of Electrical Engineers on May 30th, 31st and June 1st, was attended by nearly four hundred members from thirteen different countries, most of whom met each other informally at a reception the previous evening. The proceedings were opened by Dr Barrett (Chairman of the Hydrocarbon Research Group) and the thirty four papers presented were divided into two sections, for which Drs Martin and James provided stimulating introductory papers. Our thanks are due to them and the other session chairmen, who maintained so well the strict timetable necessitated by the crowded programme but allowed a free and vigorous discussion.

It was felt that in this rapidly growing field nomenclature and methods of presentation of data should be standardized as early as possible. A special committee was accordingly nominated to consider these matters and the Chairman, Dr Martin, presented its recommendations at the end of the symposium. The meeting concluded with a short appreciation by Dr Bradford.

We have collected, in this volume, the papers which were presented together with the discussions and nomenclature recommendations. This could not have been accomplished without the help of Mr Harbourn and Dr James in editing both papers and discussion. The effort of Mr Sell in reproducing two of the papers at very short notice was much appreciated. Finally we are indebted to Messrs Butterworths for their advice and their expeditious management of the production of both the preprints and this volume.

S. F. Birch
D. H. Desty
H. C. Rampton

July 1956

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NOMENCLATURE RECOMMENDATIONS

The Committee recommends:

(1) *Nomenclature*

(*a*) That the term 'Gas Chromatography' be used to describe all chromatographic methods in which the moving phase is a gas*. That the term 'Vapour Phase Chromatography' be no longer employed.

(*b*) That the term 'Gas–Liquid Chromatography' be used to describe all gas chromatographic methods in which the fixed phase is a liquid (distributed on an inert support).

(*c*) That the term 'Gas–Solid Chromatography' be used to describe all gas chromatographic methods in which the fixed phase is a solid (e.g. charcoal, zeolites).

(2) *Presentation of retention values in gas–liquid chromatography*

Since for many purposes it is unnecessary to determine absolute retention volumes, and since, by the use of an internal standard whose corrected retention volume per gramme of liquid phase has been measured, all values can be compared, it is recommended:

(*a*) That retention values (retention volumes or retention times of concentration maxima) should be expressed relative to an internal standard.

That in presenting values for a series of substances, the internal standard substance should be chosen so as to have a retention value near the middle of the series.

That internal standards with very low retention values should not be used.

That retention values should be corrected for dead-volume (by injection of a permanent gas) before these values are expressed relative to the internal standard.

That such results should be quoted with the exact composition of the fixed liquid phase, the nature of the support material, and the exact temperature at which the column has been operated.

That column temperatures be controlled by means of vapour jackets or circulating-fluid (liquid or air) jackets. It is felt that results obtained with a column which varies in temperature (along its length, or during the course of a run) will be of little value.

(*b*) That whenever possible the corrected retention volumes per gramme of liquid phase (i.e. V_g values) should be measured (for the internal standard), careful corrections being made for the pressure drop across the column. These values may be obtained by the following procedure:

(i) Determine the volume of gas (measured at the exit pressure of the column, and corrected to dry gas at column temperature) which has

* Note: In this report the Committee uses the term 'chromatography' only where a fixed phase is involved.

passed from the column between the emergence of the dead-volume (permanent gas) peak maximum and the peak (concentration) maximum of the internal standard.

(ii) Correct this volume for the pressure drop across the column by multiplying it by the reducing factor

$$\frac{3}{2}\frac{(p_1/p_0)^2 - 1}{(p_1/p_0)^3 - 1}$$

where p_1 is the pressure at the beginning of the column, and p_0 the pressure at the exit. The values of p_1 and p_0 should be recorded.

(iii) Divide the corrected retention volume so obtained by the weight (in grammes) of the fixed liquid phase.

NOTE: The Committee has envisaged the possibility that the measurements in sections (*a*) and (*b*) may sometimes be made by different workers. Attention is drawn to the need, in connection with the corrected retention volume, of accurate measurements of flow rate. It is not considered that rotameter readings are of sufficient accuracy for this purpose, and the use of soap-bubble or capillary flowmeters is suggested.

(*c*) That the following substances should be used as internal standards:

n-butane	naphthalene
*iso*octane (2:2:4-trimethyl pentane)	methylethyl ketone
benzene	*cyclo*hexanone
*para*xylene	*cyclo*hexanol

(*d*) That in presenting retention values for new substances, one or more of the following liquid phases should be used [temperature ranges (°C) in parentheses]:

n-hexadecane	(20 to 50)	dinonyl phthalate	(20 to 100)
squalane	(20 to 150)	dimethylformamide	(—20 to 20)
benzyldiphenyl	(80 to 150)	diglycerol	(20 to 100)

(It is hoped that these liquids will be made available in standard purity.)

That while it will be of great value if studies are made on the effects of varying the support material and the packing ratio, a mixture of 20 parts by weight of fixed liquid to 80 parts by weight of inert support (preferably 'Celite 545') be used as a standard.

(*e*) That with skew peaks the results for retention values should be extrapolated to zero sample size.

NOTE: In drawing up these recommendations the Committee has in mind low-temperature (up to 150 C) columns. It is felt that the subject of high-temperature (operated above 150 C) columns is not yet sufficiently developed to put forward rigid proposals.

(3) *Column resolution*

That column resolution be expressed in terms of theoretical plate numbers. That a theoretical plate number should always refer to a particular substance, and that the theoretical plate number of the internal standard should always be given. It is recommended that theoretical plate number should be determined by the following procedure:

Tangents (see figure) are drawn to the peak at the points of inflection. The length of base line (y) cut out by these two tangents is then measured. The length from the start of the run (i.e. including dead-volume) to the middle of this base-line section (x) is also measured. Then

$$\text{Number of theoretical plates} = 16(x/y)^2$$

(4) *Vapour detectors*

In view of the often widely differing performance characteristics of the detectors now used in gas chromatography, the Committee does not feel that it would be desirable at this stage to lay down any definite rulings on the manner in which detector sensitivities should be expressed. However, it wishes to emphasize that in describing detector performance attention should be paid to the following:

(*a*) The sensitivity should be expressed in terms of vapour concentrations rather than sample size. Details should always be given of the stability (under normal rather than favourable working conditions) of the base line, both for short periods (noise) and for long periods (drift). The sources of these instabilities should be indicated wherever possible (thus the effects of vibration may be more serious under some working conditions than under others).

(*b*) Linearity of response

(*c*) Necessity for calibration

(*d*) Response time and volume of detector

(*e*) Reproducibility

(*f*) Temperature range of operation

(*g*) Range of vapours, stressing types of vapour for which the detector is particularly suited or unsuited.

D. H. Desty
E. Glueckauf
A. T. James
A. I. M. Keulemans
A. J. P. Martin
C. S. G. Phillips

OPENING ADDRESS

J. W. Barrett
Chairman of the Hydrocarbon Research Group of the Institute of Petroleum

As Chairman of the Hydrocarbon Research Group, I would like to say a few words about this Group particularly because it is an unusual organization and does not fit too easily into any definition of a learned body, academic organization or industrial group. It is a corporate organization made up from four petroleum companies, two chemical companies, a Government department and a nationalized industry of the U.K. These eight organizations together compose the Group, and each member contributes the same amount of money annually.

The object of the group is to encourage research on hydrocarbons. It has functioned continuously since its formation in 1944 when it superseded the spectroscopic group controlled first by the Petroleum Board and later by the Ministry of Aircraft Production. It has, I think, given universities in this country considerable assistance in promoting advances in chemistry and physics concerned with hydrocarbons.

The organization is simple. The Group itself is made up of a representative from each of the bodies mentioned and is then split into three panels, each of those panels covering a particular area of scientific considerations. There is a Spectroscopy Panel, a Mass Spectrometry Panel and a Hydrocarbon Chemistry Panel. It is the last which has been responsible for organizing this Symposium.

You will note that the Hydrocarbon Research Group is connected with the Institute of Petroleum from which it gets great assistance in administration and in the care of the funds involved. However, the organization of the Symposium has been exclusively in the hands of the Hydrocarbon Chemistry Panel. The idea was first suggested by one of our Group members, Dr Bradford. It has been followed up actively, and I am sure all those who have been fortunate enough to receive a copy of the preprints will agree that a very important programme has been assembled from very many laboratories, both in this country and abroad, working in this new and active field.

Dr Birch is Chairman of this Hydrocarbon Chemistry Panel, Mr Rampton is Secretary and, as you see, Mr Desty and Mr Harbourn have been responsible for the editing. All of them have been extremely energetic in getting this Symposium going today.

We are particularly glad to have this opportunity of arranging this Symposium around a subject which was started in this country and which has been so actively followed here. Again, we are particularly glad to have as one of our Chairmen of the Sessions Dr Martin, who needs no introduction to anybody working on this subject. We are singularly fortunate in our Chairmen throughout the Symposium; all of whose names are well known in this field. It is going to be largely their responsibility to see that the papers are presented so that everyone has an opportunity of hearing them, and to organize the discussions so that a proper publication will be possible both of the papers and the ensuing discussion.

We are pleased to welcome the many visitors here, especially those from overseas.

1

TRENDS IN GAS CHROMATOGRAPHY

A. J. P. Martin

I DO not need to stress to this audience the fact that this subject is developing rapidly. It seems to have a rate of development higher than any of the other chromatographic techniques, though there has indeed been a somewhat long latent period. Now, as with the other chromatographic techniques, perhaps in particular vapour chromatography, the subject from my point of view has got entirely out of hand. In several of these fields I have had a very pleasant period when I could sit down and think and not worry very much about what anyone else was doing, in the fair certainty that I was at least well ahead. But that time has now passed, apparently, in all branches of chromatography, and in paper chromatography now it is quite impossible to read all the publications which have been produced. This is not yet true of gas–liquid chromatography, but it quite obviously will be in the very near future, and I have a feeling that it is time for me to get into a quieter subject where there is less competition.

I think my function here is to try to answer the question 'Where do we go from here?' The main lines of development are quite obviously shown by the papers discussed at this conference, and the most obvious development will undoubtedly be the new applications of existing methods to the numerous industrial problems which are waiting to be exploited in this way.

Of the new things which will have to be developed there are obviously, taking it in the widest sense, very many new column packings which will be introduced, and by the widest sense I mean both in the support and the stationary phase for the gas–liquid type of column, and in new varieties of adsorbents for the gas–solid type. I have a feeling that, so far as the support goes, we are not likely to make any very striking advances on what we have at present. I may be wrong here, but that is the field where I see least possibility of advance.

So far as new stationary phases go, there is obviously a very wide field which will no doubt be exploited continuously for a long time to come.

Another quite obvious development is in the use of higher temperatures. High temperatures give advantages not only in the fact that we can deal with heavier molecules, but also in that we can expect to push efficiencies up, though this, of course, is again limited by the particular molecule with which we are dealing.

So far the use of gas–liquid chromatography for the separation of inorganic substances has barely been touched, and I feel that there is a great field here. There is no reason why we should not run our columns at really high temperatures, 1000 or 1500 C if required, and then the use of many inorganic salts

and metals will be possible, both in stationary phases and in the mobile substances. So far nobody has wanted to do this, but I feel it will come and it will be an interesting field.

Another obvious field for advance is in the detectors. It is very little use separating substances unless you can tell what you have done when you have separated them. We have half a dozen methods of detection already in use and I do not doubt that others will come along too. It seems to me that there are two possible main lines. One is increasing the simplicity of the detector. I suppose the simplest one we have at the moment is Scott's flame apparatus. The other line is to increase its sensitivity, and that seems an easier line to develop. Perhaps somebody will find a really simple way of detecting and recording, but it certainly will require something of a stroke of genius. However, to increase the sensitivity ought not to be so very difficult, and there are two ways in which this sensitivity can be usefully increased.

It can be done for the biologists by just increasing sensitivity to total quantity. Biologists may have only a few microgrammes of material to examine, and in that case they can afford to use any kind of detector which will detect a few microgrammes, and one of the most obvious is the thermal conductivity cell run at very low pressures; in theory we can push the pressure down far below what I believe has yet been used. Then the hold-up volume of the detector becomes correspondingly less since it is the amount of gas held at s.t.p. that counts. So we should be able to work from the milligramme down to the microgramme scale. Of course, that will imply that we decrease the diameter of our column correspondingly. We shall have columns only two tenths of a millimetre in diameter, and these will carry, I believe, advantages of their own that I have no time to go into.

The other method of increasing sensitivity is increasing the sensitivity in the sense not that we cut the volume but that we increase the dilution. This will have its principal advantage for substances of high molecular weight where thermal cracking determines the maximum temperature that we can use. Then, having set our maximum temperature, the larger our molecule becomes the less we can get into vapour form and, consequently, the more sensitive our detector must be to find out what we are doing. The disadvantage of this, of course, is that we are apt to push up the retention times to very large values. But, nonetheless, it will have to be done because for many purposes gas chromatography will be the only method of handling the problem.

There is already, of course, the extremely sensitive method of the unsymmetrical vibrating reed electrometer which Mr Phillips has worked on; it is no doubt capable of further development for this type of use. But it requires a lot of work to be put into it, before it becomes a routine tool.

There is another method which I do not think has yet been suggested, which holds great promise, and that is the absorption of very long x-rays. If we use the characteristic absorption edge for a particular atom—for carbon atoms it is 43·7 Å—the analysis is specific for that element. Work has been done already by Engström [ENGSTRÖM, A. *Acta radiol., Stockh.* Suppl. LXIII, 1946], in Stockholm on the analysis of histological sections, and he has been able to detect by these means, and to estimate to 10 per cent, on a small part of a microscope slide, an amount of carbon, oxygen or nitrogen of the order of 10^{-9} 10^{-12} g. If we can work to 10^{-12} g it will keep us happy for a long

time, and I believe that the method should in fact be capable of being applied to this technique. No doubt there will be lots of headaches in getting it to work. We shall have to use apparatus with beryllium windows and everything will be evacuated except our final absorption cell, and we shall have to run with helium or hydrogen as the carrier gas.

I will now turn to the problems of the routine analyst; the question will cease to be what it has been so far, mainly one of 'How do I get such-and-such substances resolved?' but will become 'How quickly can I get such-and-such substances resolved?' I think that we shall have to work over again the theory of the performance of the columns to express them principally in terms of time. We shall have to design our columns to give the quickest possible separations rather than thinking in terms of how well we are separating.

At the present time there is no real theoretical objection to running very long columns, but life is too short and materials too expensive to use columns a mile long, although we could undoubtedly get a very fine resolution on such a column. But for long-range research problems time is not all that important, although expense frequently is. I think that we should consider making the best possible use of our chromatograms. At the present time we run a couple of substances down a chromatogram and the only part we are really using is the part which is occupied by the bands themselves. We can make much better use of the chromatogram if we re-circulate the substance back to the front again. In principle, if we have a circular column and a small pump we can go on pumping these bands round and round until they become so long that they begin eating their own tails. Obviously we have to avoid that, and there is a trick we can do to prevent it. In fact it is much easier, rather than using a circular column, to use two columns with appropriate taps and outlets and inlets so that we can push gas in at either end and run the zones from one column to the other and so on round and round. We must provide also a detecting device of negligible volume to enable us to switch at the right time. If, having run the zones into one column, we stop the gas while we raise the temperature of that column slightly, and then re-start the flow of gas and run from the hot column to the cold one, the wide bands will contract more or less as they enter the cooler column, and the concentrations will go up.

The theory is not difficult to work out, and it is obvious that contraction carried too far will nullify any separation already accomplished. Theoretically the best separation is obtained when a given zone is contracted only as much as it expanded in the previous cycle, and its length is the maximum possible.

If we neglect expansion due to pressure drop down the column, and measure the width at a standard deviations on either side of the peak, the width of a zone after passing x plates is $2a\sqrt{x}$ plates.

After contracting by a factor b the width is $2ab\sqrt{x}$ plates, and the apparent distance travelled is then b^2x plates.

If we contract after each x plates further travelled, the width after n cycles is

$$2a(b^{2n}x + b^{2n-2}x + b^{2n-4}x \ldots x)^{1/2} = 2a[x(1 - b^{2n})b^2/(1 - b^2)]^{1/2}$$

Now if we have two substances with a ratio of retention volumes of β, when

one has travelled x plates the other has travelled βx plates. The separation of peaks is $(1 - \beta)x$ plates, and after contraction is $b(1 - \beta)x$ plates.

After n cycles the separation is $xb(1 - b^n)(1 - \beta)/(1 - b)$ plates.

For large n these tend to: width $2a[xb^2/(1 - b^2)]$, separation $xb(1 - \beta)/(1 - b)$.

Now suppose each of the two columns is $\frac{1}{2}x$ plates. After a large number of cycles the attainable separation, allowing each zone to expand to x/d plates and the separation between the peaks to be $2a$ standard deviations, we have

$$\frac{x}{d} = 2a\left(\frac{xb^2}{1 - b^2}\right)^{1/2} = \frac{xb(1 - \beta)}{1 - b}$$

Hence $$(1 - \beta) = (1 - b)/bd, \quad b = [x/(4a^2d^2 + x)]^{1/2}$$

and $$x = \frac{2a^2d}{(1 - \beta) + 2d(1 - \beta)^2}$$

So that for small values of $(1 - \beta)$, $x = 2a^2d/(1 - \beta)$.

Thus, for example, to separate two substances differing in retention volume by 1 per cent, and allowing each zone to expand to 1/3 of the length of one of the columns, and to separate to 3 standard deviations, we have $a = 3$, $d = 6$, $x = 2a^2d/(1 - \beta) = 2 \cdot 9 \cdot 6/0{\cdot}01 = 10{,}800$, i.e. each column has 5,040 plates. A similar separation on a straight column would require $x = 4a^2/(1 - \beta)^2 = 360{,}000$.

In fact, by discarding the leading edge of the first band, and the trailing edge of the second band, the value of d could be much reduced, with a corresponding gain in separating power. The process would have to be controlled at all stages by the recording gear, but contraction at each cycle would be too laborious. Little loss of efficiency would result from contracting after several cycles, and the calculations are readily made as above. The fact that the pressure drops down the column results in an expansion of the zones as the pressure changes by an amount $(p_1/p_0)R_F$. Nevertheless they will be compressed by an equal amount when the carrier gas is admitted to the cold column and as far as I can see the whole effect can be neglected.

There is very little more that I want to say and that is on the subject of solution forces. From the retention values we can get the free energies of solution directly; from retention values at two different temperatures we can get the heats of solution; from the difference between these values we can get entropies, and we do not require anything else. In fact, gas chromatography is one of the best methods of collecting thermodynamic data, and I foresee that it will be used more and more for that purpose.

2

THE THERMODYNAMICS OF GAS–LIQUID CHROMATOGRAPHY

E. F. G. HERINGTON
Chemical Research Laboratory, Teddington

Gas–liquid chromatography is considered as a particular example of extractive distillation and the following fundamental relation is deduced

$$\log V_{21} \simeq \log (p_1^0/p_2^0) + \log (\gamma_{13}^0/\gamma_{23}^0)$$

where V_{21} is the relative retention volume of component 2 divided by that of component 1; p_1^0 and p_2^0 are the vapour pressures of the pure liquids 1 and 2 at the temperature employed, γ_{13}^0 and γ_{23}^0 are the activity coefficients of components 1 and 2 at infinite dilution in the binary mixtures 1, 3 and 2, 3 respectively where component 3 is the stationary phase.

Examination of the various terms in this expression using experimental data other than those obtained from vapour phase chromatography reveals the theoretical foundation for many empirical relations in current use and suggests some new methods for analysing, interpreting and interpolating experimental observations.

THE separation of a binary mixture by gas–liquid chromatography entails the use of a system of at least five components, for example the column contains an inert support, a permanent gas, a high boiling liquid and the binary mixture. Fortunately it is only necessary to consider a system containing the last three components in a thermodynamic treatment. Since the temperature employed in gas–liquid chromatography is usually lower than the critical temperatures of the three components of the system it follows that the process may be considered as a particular example of extractive distillation.

The treatment will be developed in terms of the relative retention volume V_{21} which is defined as the retention volume of component 2 divided by that of component 1. Combination of equations deduced by Consden, Gordon and Martin[1] and by James and Martin[2] yields equation (1).

$$V_{21} = (m + \alpha_2)/(m + \alpha_1) \qquad \ldots.(1)$$

where m is the area of the cross section of the mobile phase divided by the area of the cross section of the stationary phase; α_1 is the partition coefficient for compound 1 defined as the mass in grammes of component 1 per millilitre of the stationary phase divided by the mass in grammes of component 1 per millilitre of the gas phase. The partition coefficient (α_2) for component 2 is similarly defined.

In order to obtain a sharp separation of the components 1 and 2 by gas–liquid chromatography it is necessary that $m < \alpha_1$, and that $m < \alpha_2$ and

hence it follows that in practice the relation (2) is a good approximation to equation (1).

$$V_{21} \simeq \alpha_2/\alpha_1 \qquad \ldots.(2)$$

Identity (3) is exact for any single composition of the liquid mixture containing components 1, 2 and 3 provided the vapours obey the ideal gas laws.

$$\log \alpha_{123} \equiv \log (p_1^0/p_2^0) + \log (\gamma_1/\gamma_2) \qquad \ldots.(3)$$

Here α_{123} is the relative volatility ratio for components 1 and 2 in the ternary mixture 1, 2 and 3 and is defined by equation (4)

$$\alpha_{123} = (N_1^g/N_1)(N_2/N_2^g) \qquad \ldots.(4)$$

Here N_1^g and N_2^g are the mole fractions of components 1 and 2 in the vapour which is in equilibrium with the ternary liquid mixture containing N_1 and N_2 mole fractions of components 1 and 2.

In the identity (3), p_1^0 and p_2^0 are the vapour pressures of pure components 1 and 2 at the temperature employed; γ_1 and γ_2 are the activity coefficients of components 1 and 2 in the ternary mixture with the respective pure liquid components as standard states and with the concentrations expressed as mole fractions.

Now in gas–liquid chromatography the stationary phase (component 3) is present in large excess in every part of the column so that it is possible to employ the approximation (5) instead of equation (3).

$$\log \alpha_{123} \simeq \log (p_1^0/p_2^0) + \log (\gamma_{13}^0/\gamma_{23}^0) \qquad \ldots.(5)$$

Here γ_{13}^0 and γ_{23}^0 are the activity coefficients of components 1 and 2 at infinite dilution in the binary mixtures 1, 3 and 2, 3 respectively.

The 'approximately equal to' sign is used in expression (5) because this relation is exact for infinitely dilute solutions of 1 plus 2 in 3, but the equation is here applied to the very dilute (but not infinitely dilute) solutions of 1 plus 2 in 3 used in gas–liquid chromatography.

Identity (6) can be derived directly from the definitions of α_{123}, α_1 and α_2 given above.

$$\alpha_{123} \equiv (\alpha_2/\alpha_1) \qquad \ldots.(6)$$

Combination of expressions (2), (5) and (6) leads to the relation (7) which forms the basis of the present discussion.

$$\log V_{21} \simeq \log (p_1^0/p_2^0) + \log (\gamma_{13}^0/\gamma_{23}^0) \qquad \ldots.(7)$$

Relation (7) can be used to calculate the thermodynamic quantity $\log (\gamma_{13}^0/\gamma_{23}^0)$ in a very simple manner from the relative retention volume and the vapour pressures of the pure components. By measuring the relative retention volumes at different temperatures the heat quantities corresponding to $\mathrm{d}\,[\log (\gamma_{13}^0/\gamma_{23}^0)]/\mathrm{d}T$ can of course be obtained.

Expressions will now be developed to describe the separation of members of a homologous series in a gas–liquid chromatographic column and to formulate these relations the terms on the right of expression (7) will be studied using data other than those obtained from gas–liquid chromatographic experiments. Empirically it is found that equation (8) is true for most

homologous series where p^0 is the vapour pressure at $T°$ absolute of a member of the series containing n carbon atoms and where A and B are constants for a given series and temperature.

$$\log p^0 = A + Bn \qquad \ldots.(8)$$

Experimental data for the *n*-alkylbenzenes[3], *n*-paraffins[3], *n*-fatty acids[4] and *n*-alcohols[5] illustrating the application of equation (8) are shown in *Figure 1*. This correlation does not appear to be well known, for example there is no reference to it in Partington's comprehensive treatise[6].

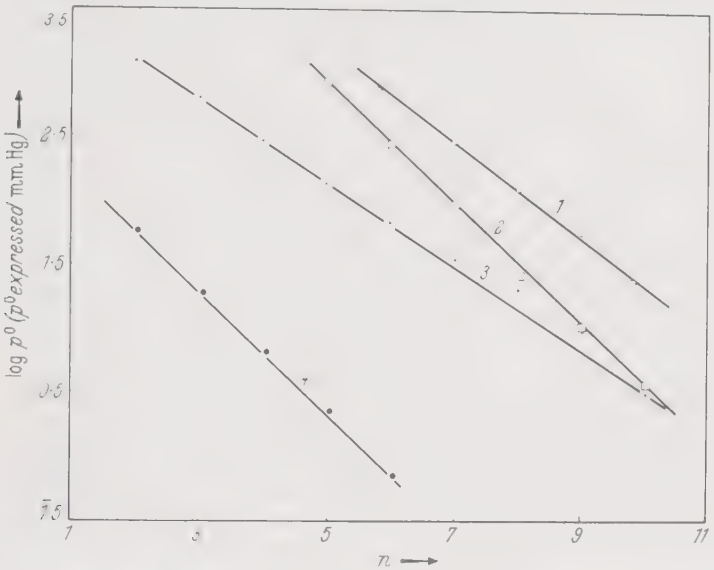

Figure 1. Log p^0 plotted against n. Curve 1, ○ *n-Alkylbenzenes, vapour pressures at* 80 C. *Curve 2,* □ n-*Paraffins, vapour pressures at* 40°C. *Curve 3,* △ n-*Fatty acids, vapour pressures at* 137°C. *Curve 4,* ● n-*Alcohols, vapour pressures at* 25°C

Search of the literature reveals that there are published values of the function γ'^0 for two series of binary mixtures containing homologues where γ'^0 is the activity coefficient of the component in high dilution. Examination of the results due to Butler, Thomson and McLennon[7] for very dilute solutions of alcohols in water and of the results due to Andon, Cox and Herington[8] for very dilute solutions of pyridine bases in water shows that equation (9) is true.

$$\log \gamma'^0 = C + Dn \qquad \ldots.(9)$$

where n is the number of carbon atoms in the molecule, C and D are constants for a given homologous series, solvent and temperature. Such a relation is to be expected on theoretical grounds and should apply to solvents other than water.

Insertion of equations (8) and (9) into (7) yields (10)

$$\log V_{21} \simeq (\log p_1^0 \gamma'^0_{13}) - (A + C) - (B + D)n_2 \qquad \ldots.(10)$$

where n_2 is the number of carbon atoms in component 2.

Several methods of plotting gas–liquid chromatographic data for homologous series in current use are special cases of expression (10). For example this can be written in the form (11).

$$\log V_2 \simeq (\log p_1^0 \gamma_{13}^0 V_1) - (A + C) - (B + D)n_2 \qquad \ldots.(11)$$

From this it follows that the plot of log V_2 against n_2 should yield a straight line where V_2 is the retention volume of component 2. This plot has been recognized for some time as a useful one (e.g. see the results for a series of *n*-fatty acids and of *iso*-fatty acids plotted on *Figure 12*, ref. 2, and the results for homologous series of paraffins, alcohols, formates, acetates, propionates and methylketones presented in *Figure 4*, ref. 9). Alternatively the relative retention volumes can be employed when it follows from equation (10) that the plot of log V_{21} against n_2 for a homologous series should yield a straight line if all the relative retention volumes are calculated with respect to the same component 1. This method of plotting experimental data has also been employed (e.g. see the results for amines plotted in *Figure 2*, ref. 10).

For any homologous series it is possible to rearrange approximation (7) using equations (8) and (9) and thus obtain relation (12).

$$\log V_{21} \simeq A_1 - a_1 \log p_2^0 \qquad \ldots.(12)$$

where $A_1 = (\log p_1^0\gamma_1^0) - C + (AD/B)$ and $a_1 = 1 + (D/B)$.

Hence the plot of log V_2 against log p_2^0 or the plot of log V_{21} against log p_2^0 for a homologous series of components 2 should yield straight lines. Indeed this method of plotting data is often to be preferred to the method of plotting experimental results suggested by relation (10). A graph related to the plot of log V_2 against log p_2^0 has been discussed by Hoare and Purnell[11].

In some instances it is more convenient to correlate log V_{21} with the normal boiling points of the substances. Empirically it was found that equation (13) is true for many homologous series

$$\log p^0 = b - ct \qquad \ldots.(13)$$

where t is the normal boiling point in degrees Celsius of the member of the series which exhibits a vapour pressure p^0 at the temperature considered; b and c are constants for a given homologous series and temperature. *Figure 2* illustrates how well certain experimental measurements fit equation (13). The source of the data used in *Figure 2* was the same as that used in *Figure 1* except that the normal boiling points of the alcohols were taken from Stull[4].

Combination of expressions (12) and (13) yields (14)

$$\log V_{21} \simeq A_2 + a_2 t \qquad \ldots.(14)$$

where $A_2 = A_1 - a_1 b$ and $a_2 = a_1 c$.

Thus the logarithms of the retention volumes for the members of a homologous series plotted against the normal boiling points should yield a straight line. This method of plotting experimental results has been used by Sullivan, Lotz and Willingham[12].

The relationship between the relative retention volumes ($V_{21\,\mathrm{I}}$ and $V_{21\,\mathrm{II}}$) for members of a homologous series passed through two columns, one containing stationary phase I and the other containing stationary phase II, will now be considered. Combination of expressions (7) and (9) lead to relation (15).

$$\log (V_{21\,\mathrm{I}}/V_{21\,\mathrm{II}}) \simeq A_3 + a_3 n_2 \qquad \ldots.(15)$$

where $A_3 = (C_{1\,I} + D_{1\,I}n_1) - (C_{1\,II} + D_{1\,II}n_1) + (C_{2\,II} - C_{2\,I})$ and $a_3 = (D_{2\,II} - D_{2\,I})$. Here $C_{1\,I}$, $D_{1\,I}$, $C_{1\,II}$, $D_{1\,II}$, $C_{2\,I}$, $D_{2\,I}$, $C_{2\,II}$ and $D_{2\,II}$ are the constants in equation (9) for the appropriate components 1 and 2 and for third components

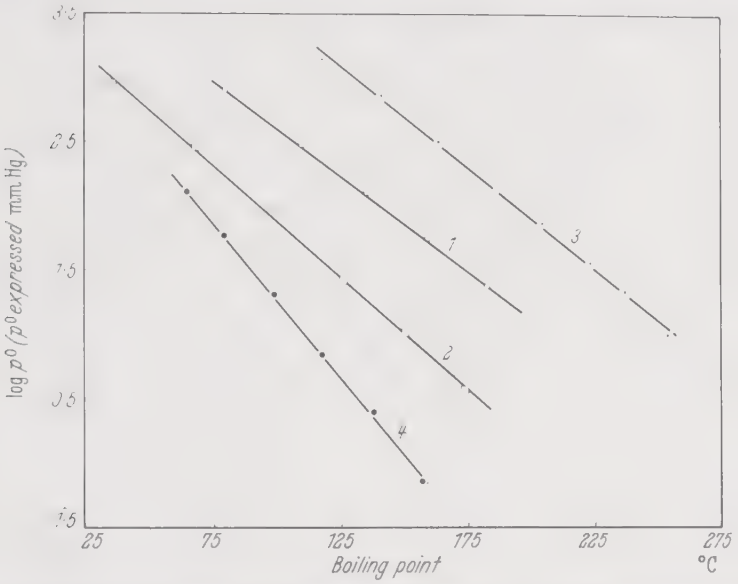

Figure 2. log p^0 *plotted against boiling point. Curve 1,* ○ n-*Alkylbenzenes, vapour pressures at* 80°C. *Curve 2,* □ n-*Paraffins, vapour pressures at* 40°C. *Curve 3,* × n-*Fatty acids, vapour pressures at* 137°C. *Curve 4,* ● n-*Alcohols, vapour pressures at* 25°C

I and II; n_1 and n_2 are the numbers of carbon atoms in components 1 and 2.

From relation (15) it follows that the plot of log $(V_{2\,I}/V_{2\,II})$ against n_2 should yield a straight line. A plot of this type constructed from published

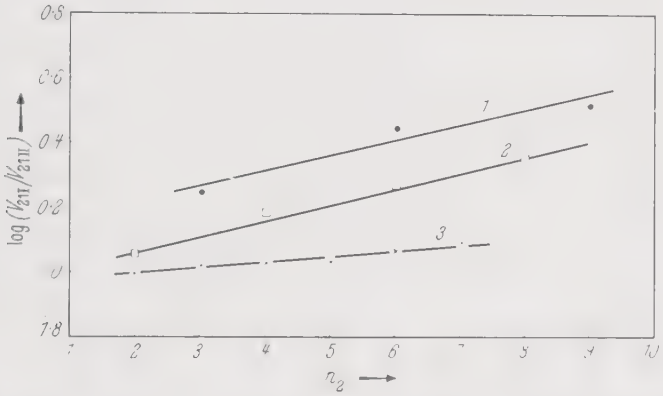

Figure 3. log $(V_{2\,I}/V_{2\,II})$ *plotted against* n_2. *Curve 1,* ● *Tertiary straight chain amines Curve 2,* □ *Secondary straight chain amines. Curve 3,* · *Primary straight chain amines*

measurements of the relative retention volumes of aliphatic amines[10] is shown in *Figure 3*. In *Figure 3* component 1 is ethylamine, solvent I is paraffin and solvent II is Lubrol MO.

A further approximation is possible if the stationary phases I and II are both weakly polar liquids (e.g. paraffin and Lubrol MO) because then a_3 may

be very small numerically and hence approximation (15) can be written as (16).

$$V_{21\,\mathrm{I}} \approx 10^{A_3} V_{21\,\mathrm{II}} \qquad \ldots.(16)$$

where the sign $\approx$ is used to emphasize that a rough approximation has been made. James has plotted $V_{21\,\mathrm{I}}$ against $V_{21\,\mathrm{II}}$ using experimental measurements on aliphatic amines and has obtained straight lines as required by relation (16) (see *Figure 3*, ref. 10). Under these conditions it follows that if components 1 and 2 belong to the same homologous series then A_3 will be numerically small so that for these special circumstances expression (17) will be approximately true.

$$V_{21\,\mathrm{I}} \approx V_{21\,\mathrm{II}} \qquad \ldots.(17)$$

Experimental results show that this relation is often obeyed approximately, for example the plot of measurements for aliphatic primary amines with the relative retention volume of ethylamine equal to unity (*Figure 3*, ref. 10), and the plot of the results for normal paraffins with the relative retention volume of *n*-pentane equal to unity (*Figure 11*, ref. 13) are straight lines at an angle of approximately 45° to the axis.

The suggestion has been made that the graph of $V_{21\,\mathrm{I}}$ plotted against $V_{21\,\mathrm{II}}$ might be used for the identification of functional groups (ref. 14) but the present theoretical treatment suggests that this method of plotting might not always yield good straight lines if one or both of the stationary phases (I or II) were strongly polar liquids. The theory suggests that in general it would be better to use expression (18) which can be obtained by means of relation (12).

$$\log V_{21\,\mathrm{I}} \simeq A_4 + a_4 \log V_{21\,\mathrm{II}} \qquad \ldots.(18)$$

where $A_4 = A_{1\,\mathrm{I}} - (a_{1\,\mathrm{I}}/a_{1\,\mathrm{II}})A_{1\,\mathrm{II}}$ and $a_4 = a_{1\,\mathrm{I}}/a_{1\,\mathrm{II}}$.

Here $A_{1\,\mathrm{I}}$, $a_{1\,\mathrm{I}}$, $A_{1\,\mathrm{II}}$ and $a_{1\,\mathrm{II}}$ are the constants in relation (12) for component 1 in stationary phases I and II. Relation (18) suggests that the plot of $\log V_{21\,\mathrm{I}}$ against $\log V_{21\,\mathrm{II}}$ should yield a straight line and *Figure 4* shows a plot of these quantities calculated from the experimental results for aliphatic amines given in ref. 10. In *Figure 4* component 1 is ethylamine, stationary phase I is paraffin and stationary phase II is Lubrol MO. This method of plotting is superior in every way to that suggested by relation (16), for not only is the relation (18) of greater generality but the points on the new plot are evenly spaced for successive members of the series. This equal spacing of points, which is a direct result of the existence of relations (8) and (9), makes it very easy to interpolate the data. For example, the values of the logarithms of the relative retention volumes of dimethylethylamine, methyldiethylamine, diethylpropylamine and ethyldipropylamine in paraffin and in Lubrol MO can be read from the points marked *w*, *x*, *y* and *z* on *Figure 4*. The ease with which this information can be obtained from *Figure 4* should be contrasted with the difficulty of extracting the same information from *Figure 3*, ref. 10.

The expressions (8)–(18) have been concerned with the behaviour of homologous series in gas–liquid chromatography but now the choice of a suitable immobile phase will be considered. Usually the stationary phase will be chosen so that the term $\log (\gamma'^{0}_{13}/\gamma'^{0}_{23})$ is of the same sign as the term $\log (p^{0}_{1}/p^{0}_{2})$ and thus the effect of the deviation of the solution from ideality and

the effect of vapour pressure are made to reinforce each other. In special circumstances it may be desirable to choose a solvent so that the function $\log (\gamma_{13}^0/\gamma_{23}^0)$ is predominant and of opposite sign to $\log (p_1^0/p_2^0)$. For example, these conditions exist in the column containing silver nitrate which is recommended for the estimation of ethane in ethylene (Bradford, Harvey and Chalkley[15]).

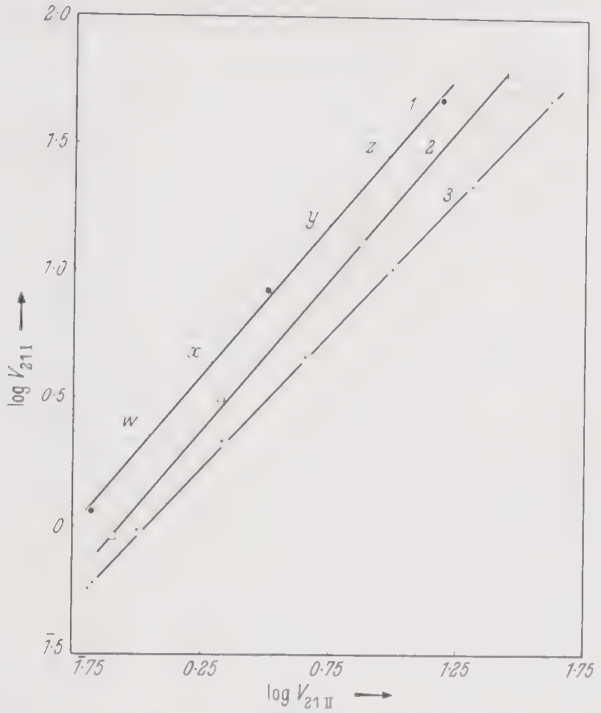

Figure 4. $\log V_{211}$ *plotted against* $\log V_{21\,II}$. *Curve 1,* ● *Tertiary straight chain amines. Curve 2,* □ *Secondary straight chain amines. Curve 3,* ○ *Primary straight chain amines*

The term $\log (p_1^0/p_2^0)$ may be numerically small for some pairs of liquids and then it may not be possible to choose a stationary phase which makes $\log (\gamma_{13}^0/\gamma_{23}^0)$ large if the components 1 and 2 have similar chemical structures. Pairs of liquids of this type are *m*- and *p*-xylene (b.pt 139·1 and 138·3°C respectively) and β- and γ-picoline (b.pt 144·1 and 145·4°C respectively). This difficulty also arises in extractive distillation and has caused Ju Chin Chu, Kharbanda, Brooks and Wang[16] to state that it is not possible to separate *m*- and *p*-xylene by distillation. Although the complete separation of such liquid pairs may be difficult by gas–liquid chromatography some separation can usually be achieved if very long columns with an enormous number of theoretical plates are employed.

Two components of different chemical classes can usually be separated easily by gas–liquid chromatography for even if $|\log (p_1^0/p_2^0)|$ is small it is usually possible to choose a solvent which makes $|\log (\gamma_{13}^0/\gamma_{23}^0)|$ large; thus, for example, a mixture of benzene (b.pt 80·1°C) and *cyclo*hexane (80·7°C) can be analysed readily.

Several plasticizers (e.g. phthalate esters) have been used already as stationary phases in gas–liquid chromatography and it is probable that other

members of this class of substance will be used in the future (see *Plasticizers*[17] for a valuable summary of the properties of this class of material). Ewell, Harrison and Berg[18] have published a useful classification of liquids which allows the deviations from ideality of some mixtures to be predicted. There is, however, much room for further work on the choice of solvents and complexing agents suitable for specific separations by gas–liquid chromatography.

The work described in this paper forms part of the programme of the Chemistry Research Board and is published by permission of the Director, Chemical Research Laboratory.

Symbols

A	Constant in the equation $\log p^0 = A + Bn$
A_1	Constant defined by the equation $A_1 = (\log p_1^0 \gamma_{13}^0) - C + (AD/B)$
A_2	Constant defined by the equation $A_2 = A_1 - ab$
A_3	Constant defined by the equation $A_3 = (C_{1\,\mathrm{I}} + D_{1\,\mathrm{I}} n_1) - (C_{1\,\mathrm{II}} + D_{1\,\mathrm{II}} n_1) + (C_{2\,\mathrm{II}} - C_{2\,\mathrm{I}})$
A_4	Constant defined by the equation $A_4 = A_{1\,\mathrm{I}} - (a_{1\,\mathrm{I}}/a_{1\,\mathrm{II}}) A_{1\,\mathrm{II}}$
$A_{1\,\mathrm{I}}$	Constant A_1 for stationary phase I
$A_{1\,\mathrm{II}}$	Constant A_1 for stationary phase II
a_1	Constant defined by the equation $a_1 = 1 + (D/B)$
a_2	Constant defined by the equation $a_2 = a_1 c$
a_3	Constant defined by the equation $a_3 = (D_{2\,\mathrm{II}} - D_{2\,\mathrm{I}})$
a_4	Constant defined by the ratio $(a_{1\,\mathrm{I}}/a_{1\,\mathrm{II}})$
$a_{1\,\mathrm{I}}$	Constant a_1 for the stationary phase I
$a_{1\,\mathrm{II}}$	Constant a_1 for the stationary phase II
B	Constant in the equation $\log p^0 = A + Bn$
b	Constant in the equation $\log p^0 = b - ct$
C	Constant in the equation $\log \gamma^0 = C + Dn$
$C_{1\,\mathrm{I}}, C_{1\,\mathrm{II}}$ / $C_{2\,\mathrm{I}}, C_{2\,\mathrm{II}}$	Constant C for components 1 and 2 in stationary phases I and II
c	Constant in the equation $\log p^0 = b - ct$
D	Constant in the equation $\log \gamma^0 = C + Dn$
$D_{1\,\mathrm{I}}, D_{1\,\mathrm{II}}$ / $D_{2\,\mathrm{I}}, D_{2\,\mathrm{II}}$	Constant D for components 1 and 2 in stationary phases I and II
m	Area of cross section of mobile phase divided by the area of cross section of the stationary phase
N_1, N_2	Mole fractions of components 1 and 2 in ternary liquid mixtures of components 1, 2 and 3
N_1^g, N_2^g	Mole fractions of components 1 and 2 in the vapour in equilibrium with the ternary liquid mixture containing N_1 and N_2 mole fractions of 1 and 2
n	Number of carbon atoms in the molecule
n_1	Number of carbon atoms in the molecule of component 1
n_2	Number of carbon atoms in the molecule of component 2
p^0	Vapour pressure of a pure liquid

p_1^0, p_2^0	Vapour pressures of pure components 1 and 2 respectively
t	Normal boiling point in degrees Celsius
V_1	Retention volume of component 1
V_2	Retention volume of component 2
V_{21}	Retention volume of component 2 divided by the retention volume of component 1
$V_{21\,\mathrm{I}}$	Retention volume of component 2 divided by the retention volume of component 1 in the presence of stationary phase I
$V_{21\,\mathrm{II}}$	Retention volume of component 2 divided by the retention volume of component 1 in the presence of stationary phase II
α_1, α_2	The partition coefficient, α_1, is defined as the mass in grammes of component 1 per millilitre of the stationary phase divided by the mass in grammes of component 1 per millilitre of the gas phase. The partition coefficient for component 2 is similarly defined
α_{123}	Relative volatility ratio for components 1 and 2 in the ternary mixture 1, 2, 3
γ'^0	Activity coefficient of a component at infinite dilution in binary mixture with component 3
γ_1, γ_2	Activity coefficients of components 1 and 2 in the ternary mixture of components 1, 2 and 3 of any given composition
γ_{13}^0, γ_{23}^0	Activity coefficients of components 1 and 2 at infinite dilution in the binary solutions containing 3, with pure liquid components 1 and 2 as the standard states and with the compositions expressed as mole fractions

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DISCUSSION

C. L. DUNN: I should like to compliment the programme committee for having chosen this contribution by Dr Herington as the first paper of this symposium. It is essential to have an understanding of the thermodynamics of gas–liquid partition chromatography if one is to obtain maximum benefit from the use of this technique, but unfortunately many people lack this understanding. In this paper Dr Herington makes use of a correlation between activity coefficient at infinite dilution and the number of carbon atoms in a homologous series of solutes based on the data of Butler *et al.* At the same time Dr Herington expresses a desire that more such data be available. It happens that my associates at Shell Development have considerable data of this kind and will publish a large proportion in the coming months in publications of the American Chemical Society.

Dr Herington uses a linear relationship between γ' and n, the number of carbon atoms, and states that such a relation is expected on theoretical grounds. Personally I see no theoretical basis for this linear relationship and experimentally it is found to hold only in very special cases. I am sure that many of you have observed that in correlations of retention volumes with carbon number the lower members of a series usually do not fall into line. We have plotted the infinite dilution for a series of normal paraffins in several solvents. For this very special solute which has no functional n polar group the relationship is linear except for a term $D(n_1 - n_2)^2$ which expresses the interaction between CH_2 and CH_3 groups of the solute and solvent molecules. Only with water which has no C atoms does this relationship become linear. As we proceed to a solute other than normal paraffins we find that the role of the functional or polar group in the solute is to introduce a curvature at the lower end expressed by a term $1/n_1$. The overall effect of these activity coefficient relationships not being linear is of course that in many plots of retention volumes (based on a linear relationship) lower members of a series can be expected to fall out of line.

From similar studies it is known that branching in a molecule usually has only a small effect on the activity coefficient. However, it is known that branching affects vapour pressure. Thus when one considers retention volumes, which involve a product of γ' and p^0, one finds that both the position and the amount of branching have large effects and branched compounds behave differently compared with straight-chain compounds of similar carbon number.

3

FACTORS DETERMINING COLUMN EFFICIENCY IN GAS–LIQUID PARTITION CHROMATOGRAPHY

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An equation developed by van Deemter, Zuiderweg and Klinkenberg for the efficiency of the column in 'linear non-ideal' chromatography is considered, and the influence on the efficiency caused by varying the parameters of this equation are discussed with reference to gas–liquid partition chromatography. Some of the conclusions so drawn—which have been confirmed and extended by experimental data—are as follows.

(*1*) As support for the stationary liquid, an extremely finely divided solid gives a somewhat lower efficiency than a more coarsely granulated material, such as a narrow screen fraction between 30 and 80 mesh.

(*2*) A factor of extreme importance is the relation between the carrier gas velocity and the ratio of inlet to outlet pressures of the column. Very low gas rates, for instance, can sometimes seriously impair column efficiency.

(*3*) A low column temperature is (with certain restrictions) a favourable factor.

(*4*) The amount of stationary liquid on the support should not be too high or too low. 15–20 per cent is generally a satisfactory proportion.

(*5*) The relative value of hydrogen or helium as carrier gas with respect to more viscous gases (nitrogen or carbon dioxide) is complex, but for high efficiencies the latter are generally preferable.

FOR the treatment of chromatographic processes in which the distribution follows a linear distribution isotherm the theoretical plate concept has been very fruitful. This concept was introduced into chromatography by Martin and Synge[1] in 1941. It was re-examined by Mayer and Tompkins[2], who expanded the theory so as to render possible a calculation of the number of 'theoretical plates' needed to obtain a required purity of the separated products.

The plate concept accounts for the shape of the elution curves usually obtained in partition chromatography, but does not enter into the mechanisms that give rise to their particular gaussian shape. In their model Mayer and Tompkins visualized chromatography as a discontinuous process, in which a finite volume of solution is equilibrated successively, step by step, with a number of theoretical plates full of sorbent. A shortcoming in this model was discussed by Glueckauf[3]. The step-by-step equilibration leads to a binomial distribution, whereas continuous flow leads to a distribution of the Poisson type. It is true that for a sufficiently large number of equilibrations both

distributions closely approximate to gaussian curves, but their widths are different, as was shown by Klinkenberg and Sjenitzer[4].

These authors observe that many mechanisms will account for the gaussian distributions occurring, for instance, in partition chromatography. The fact that a certain mechanism agrees with such a distribution is therefore no proof of its validity. For such a proof a single experiment is not sufficient.

The mechanisms causing the widening of a band in chromatography have been examined by van Deemter, Zuiderweg and Klinkenberg[5]. They developed the 'rate theory' for linear non-ideal chromatography. This theory is a valuable extension of that developed by Glueckauf[6] and other investigators.

With the 'plate' theory the number of theoretical plates in a given system can be calculated. From this number and from the length of the column the height equivalent to a theoretical plate (HETP) is found. In the 'rate theory' the HETP is brought into relation with the actual phenomena occurring in a chromatograph column. A combination of the plate theory and the rate theory renders it possible to enter into at least a qualitative, but sometimes even a more or less quantitative, discussion of the numerous parameters operating in gas–liquid partition chromatography (GLPC).

A brief outline of the rate theory will be given, by first dealing with ideal chromatography, then examining the causes of deviation from ideality and finally giving an expression derived by van Deemter *et al.* for the HETP as a function of the parameters involved.

A few experiments will be described to illustrate how closely the theory agrees with the phenomena.

Ideal Chromatography

Chromatography is a physical method of separation in which the components to be separated distribute themselves as solutes between two phases. One of

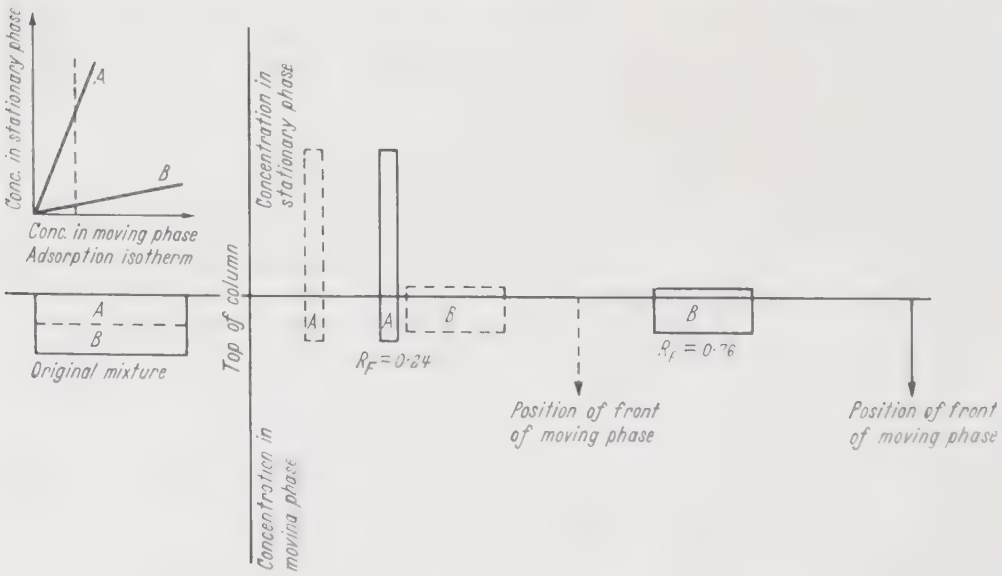

Figure 1. Schematic diagram of linear ideal chromatography (after A. J. P. Martin Endeavour **6**, 22, 1947)

these phases, which has a high surface to volume ratio, is stationary and the other percolates through it.

In 'ideal' chromatography the following conditions are postulated:

(*a*) The proportion of the two phases at all points of the column is constant

(*b*) The flow of the mobile phase is uniform

(*c*) Molecular diffusion of solute molecules in axial direction does not occur in either of the two phases

(*d*) Equilibrium between the two phases is instantaneous.

If furthermore the partition coefficient of the solutes does not depend upon the concentration (i.e. if the distribution isotherm is linear) we speak of 'linear ideal' chromatography. From a band of solute introduced into the column all concentrations travel at the same rate. For any solute this rate stands in a constant proportion (R_F) to the rate of the mobile phase. As a consequence a band preserves its shape during its passage through the column. This case has been depicted schematically in *Figure 1*; it has been treated by Wilson[7] and others.

Linear Non-ideal Chromatography

In reality chromatography is neither ideal nor linear. For the low concentrations of vapour usually encountered in GLPC, however, we can still assume a linear isotherm, so that a 'linear non-ideal' treatment is permissible, at all events for small amounts of solutes. The conditions referred to under 'ideal chromatography' are now affected as follows.

(*i*) Of those postulated, only the first is fulfilled in practice, provided at least that the column has been properly packed.

(*ii*) Uniformity of flow is departed from in two ways in GLPC.

First, there is a pressure gradient along the length of the column, as a consequence of which the linear carrier gas velocity increases from the column inlet to the column outlet. This non-uniformity, however, affects all solute molecules to the same extent and hence does not cause band broadening.

Secondly, as a result of the presence of the packing, gas molecules travel through the column along many different paths. These paths have unequal lengths; also, the velocity is not axially directed and it furthermore depends on the width of the voids between the particles. These effects cause the residence time of gas molecules (and hence also of solute molecules) in the column to spread; the result is that there is a depletion and widening of a band. This widening depends upon the size of the particles that constitute the packing, their shape and the manner in which they have been packed.

This mechanism of band broadening is termed 'eddy diffusion' on account of its analogy to eddy diffusion in turbulent flow.

(*iii*) Molecular diffusion is superimposed on the forced carrier gas velocity and tends to enhance or counteract the transport of the solute molecules. (The corresponding effect in the liquid phase is negligible.) Molecular diffusion is the second mechanism of band broadening.

(*iv*) The last condition requires instantaneous equilibrium or an infinite rate of mass transfer between the two phases. This condition is quite invalid for the high rates of flow operative in GLPC, although the high dispersion of the liquid phase is a very effective means of enhancing the establishment of equilibrium. A consequence of the finite rate of mass transfer is that solute

molecules either fail to go into solution and then travel somewhat ahead of the band, or are slow in getting into the moving phase and then lag behind the band. The resistance to mass transfer is the third important factor causing band broadening.

It will be seen that of the three mechanisms discussed, eddy diffusion does not depend upon the flow rate, at least at those velocities normally encountered in GLPC.

Molecular diffusion has a large effect at low rates of flow (long retention times); the effect is inversely proportional to the linear gas velocity. The resistance to mass transfer increases at increasing gas rates.

Equation for the HETP

The above-mentioned mechanisms of band broadening have been discussed by Klinkenberg and Sjenitzer[4] and by van Deemter, Zuiderweg and Klinkenberg[5]. The latter authors derived a basic equation for the HETP in a GLPC column. This expression reads:

$$H = \underbrace{2\lambda d_p}_{\text{contribution of eddy diffusion due to packing}} + \underbrace{\frac{\gamma D_{gas}}{u}}_{\text{contribution of molecular diffusion}} + \underbrace{\frac{8}{\pi^2} \cdot \frac{k'}{(1+k')^2} \cdot \frac{d_f^2}{D_{liq.}} \cdot u}_{\text{contribution of resistance to mass transfer}} \quad \ldots\ldots(1)$$

where H = HETP; λ = a quantity characteristic of the packing; d_p = average particle diameter; γ = a correction factor accounting for the tortuosity of the gas channels; D_{gas}, $D_{liq.}$ = diffusivity in the gas phase and liquid phase respectively; u = linear gas velocity in the packed column (u_i at column inlet, u_o at column outlet); $k' = K(F_{liq.}/F_{gas})$, where K = partition coefficient of the solute, expressed as the ratio of moles per unit volume of liquid phase to moles per unit volume of gas phase; $F_{liq.}$ and F_{gas} = fraction of cross section occupied by liquid and gas phase respectively; and d_f = 'effective' thickness of the liquid film with which the particles of the support are coated.

In the derivation of this formula it has been assumed that the resistance to mass transfer is fully located in the liquid phase, an assumption which seems permissible in view of the high diffusivity in the gas phase compared to that in the liquid phase. If we rewrite this equation in a simpler form as

$$H = A + B/u + Cu \quad \ldots\ldots(2)$$

we see that it is the equation of a hyperbola with a minimum $A + 2(BC)^{\frac{1}{2}}$ at $u = B/C^{\frac{1}{2}}$. This means that there is one value of u at which the column is operating under the most efficient gas velocity. It should be observed, however, that owing to the compressibility of the gas phase, u is not constant over the column, but gradually increases from inlet to outlet. Hence only a very small section can operate at maximum efficiency.

Figure 2 represents a hypothetical case of a curve for H versus u, but one that might well occur in practice. It is a plot of equation (2) in which we have taken:

$$A = 0{\cdot}1\text{cm},\ B = 0{\cdot}30\ \text{cm}^2/\text{sec},\ C = 0{\cdot}05\ \text{sec},\ \text{so that}$$
$$H = 0{\cdot}1 + 0{\cdot}30/u + 0{\cdot}05u \quad \ldots\ldots(2a)$$

The minimum HETP is 0·345 cm at $u = 2{\cdot}45$ cm/sec.

The area below the curve may be divided into three sections corresponding to the three terms of equations (1) or (2):

I area of eddy diffusion
II area of mass transfer
III area of molecular diffusion.

At low gas velocities the HETP is mainly controlled by molecular diffusion. At high gas velocities the contribution of the molecular diffusion, on the other

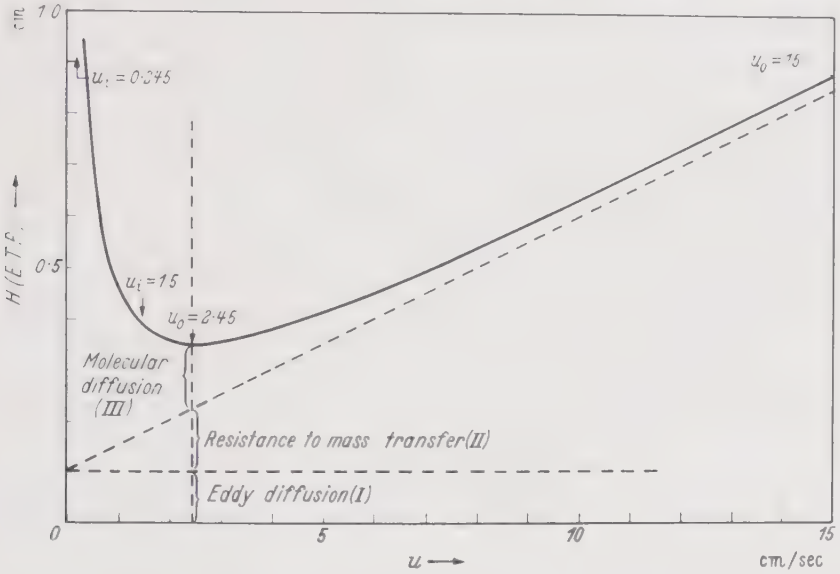

Figure 2. Plot of HETP against linear gas velocity (calculated).
(Gas diffusion and mass transfer are both appreciable)

hand, is almost negligible; the HETP is now almost entirely controlled by the resistance to mass transfer. The contribution of eddy diffusion does not depend on the gas velocity.

In order to estimate how the HETP may change from point to point in the column we must consider how u changes in the column.

In *Figure 3* three curves have been drawn; they represent the gas velocity in the column relative to that at the column outlet (u/u_o) as a function of the fractional distance x in the column, for three values of p_i/p_o (ratios of inlet to outlet pressure).

It should be observed that at $p_i/p_o = 10$ the major part of the column operates at a gas velocity not much different from that at the inlet; in the very last part of the column the gas velocity increases rapidly to the value u_o. Corresponding to this case, the area in which a column operates at $u_i = 1{\cdot}5$ cm/sec and $u_o = 15$ cm/sec has been indicated in *Figure 2*. At the column inlet the HETP is 0·39 cm and at the outlet 0·87 cm. The optimum value of u, 2·45 cm/sec, is reached at $x = 0{\cdot}63$ ($u/u_o = 0{\cdot}63$), hence the first 63 per cent of the column operates at values of HETP between 0·39 and 0·345 cm and here the average HETP is not much higher than the minimum. If, however, we had taken the gas velocity at the *outlet*, u_o, as 2·45 cm/sec (the

optimum of the curve), then u, would become 0·245 cm/sec and the major part of the column would be operating in the area where the HETP is seriously affected by molecular diffusion.

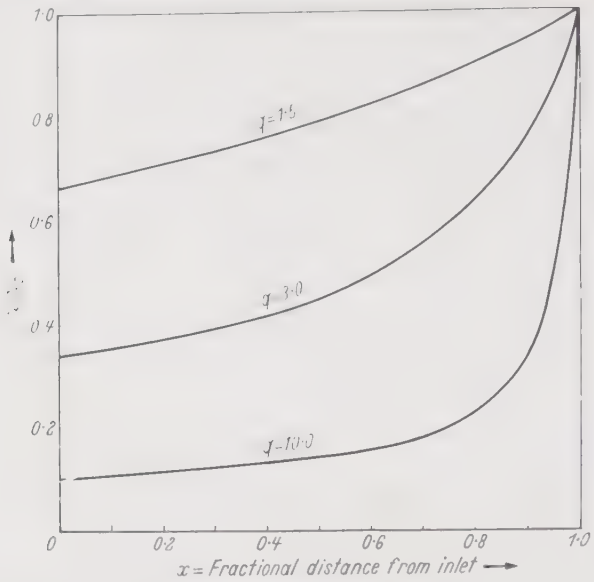

Figure 3. Plot of u/u_o against x for various values of q (where $q = p_i/p_o$)

Interpretation of the Coefficients A, B and C

From equation (2) and from *Figure 2* it follows that the HETP is the sum of three (almost) independent terms. In order to obtain high column efficiencies it is advisable not only to employ appropriate gas velocities, but also to find means of making the three terms in equation (1) as small as possible. The possibility of effecting an improvement is illustrated by the very favourable curve shown in *Figure 4*, which was drawn for $A = 0{\cdot}1$ cm,

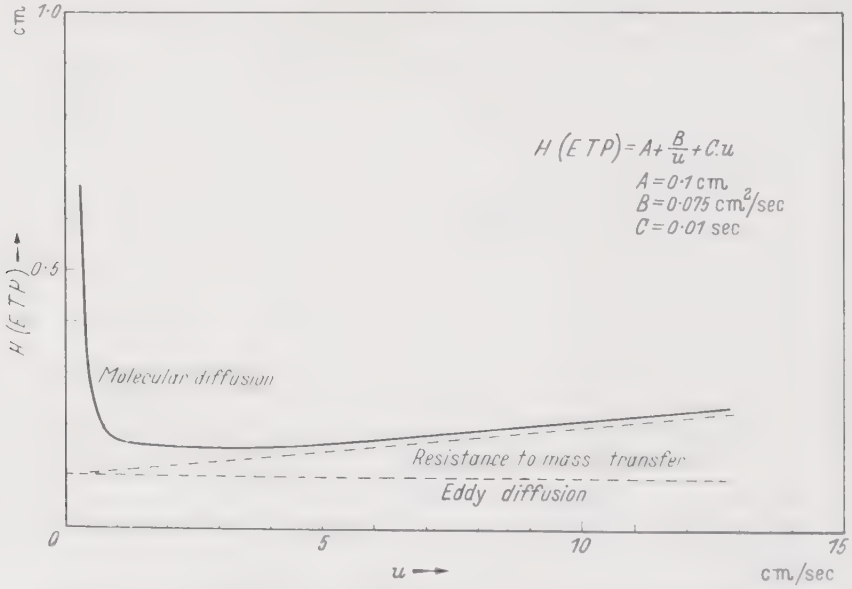

Figure 4. Calculated curve for H against u (gas diffusion and mass transfer resistance are both small)

$B = 0{\cdot}075$ cm^2 sec and $C = 0{\cdot}01$ sec and which has a minimum of $H = 1{\cdot}55$, that is to say less than half the minimum of the previous examples.

Means to decrease the three terms in equation (1) and values usually encountered for A, B and C will now be discussed.

1. The term $2\lambda d_p$; the eddy diffusion term

This term is characteristic of the column packing and does not depend upon the properties of solute, solvent or operating conditions. The most obvious means of decreasing this term would seem to lie in using smaller particles. The value of λ, however, characterizes the manner in which the particles of the support have been packed. The usual method of preparation is first to coat the support with the stationary liquid and then fill the column.

Celite (a diatomaceous earth marketed by Johns Manville) is the support most frequently used. When size-graded according to the procedure described by James and Martin[8] the average particle diameter is about 40μ. According to the present author's experience it is extremely difficult to pack a column with this material once it has been wetted with the stationary liquid. High values of λ then result. In the article by van Deemter *et al.*[5], columns packed with Celite (300–400 mesh or $d_p = 40\mu$) were compared with columns packed with a much coarser material, namely a 50/80 ASTM sieve fraction of a ground firebrick (Sterchamol*) with an average particle diameter of about 250μ. The value of $2\lambda d_p$ was the same for these two columns, viz. about 1 mm, corresponding with a value of λ of approximately 12 for Celite and $\lambda \sim 2$ for the coarse particles.

It seems reasonable to expect that regular packing is easier to realize with large than with small particles. According to Klinkenberg and Sjenitzer, normal values are $\lambda \sim 8$ for 200–400 mesh (74–37μ), $\lambda \sim 3$ for 50–100 mesh (297–149μ), $\lambda \sim 1$ for 20–40 mesh (840–420μ). The high value of λ with Celite may point to channelling. From the above it follows that it is not easy to take full advantage of a fine support such as Celite. Experimentally it has been found that for analytical columns of $\frac{1}{4}$-inch diameter the most efficient packing was obtained with 30–50 or 50–80 mesh particles (or with other not too wide screen fractions between 30 and 80 mesh). With still coarser particles the slight decrease in λ does not make up for the increase in d_p. In our experience values of $2\lambda d_p = 0{\cdot}1$ cm are attainable with comparative ease.

A suggestion that has not yet been worked out is to fill the column with a dry support of small particle size, which then can probably be packed with greater regularity, and to impregnate the packing *in situ* with the liquid. It is not unlikely that values of $2\lambda d_p$ lower than 0·1 cm may then be obtained, although the authors believe that a value of 0·05 cm will be difficult to realize in GLPC. (In liquid–liquid partition chromatography the situation appears to be much more favourable.)

An additional advantage of employing relatively coarse packing materials is their high permeability, as a consequence of which high gas velocities may be used with but low pressure gradients.

* Sterchamol No. C-22 is a proprietary brand of furnace insulating brick manufactured in Germany. A similar material Sil-O-Cel is C_{22} firebrick, manufactured by Johns Manville.

2. The term $\gamma D_{gas}/u$; the molecular diffusion

In this term D_{gas} is the diffusivity of the solute molecules in the carrier gas; this is a property of both solute and carrier gas. D_{gas} may be influenced by the choice of the carrier gas and by the pressure. The rate of molecular diffusion is high in hydrogen and helium as compared with that in nitrogen and carbon dioxide, the gases most frequently employed. Diffusion decreases with increasing pressure of the carrier gas. The presence of the packing counteracts the molecular diffusion to a certain extent. This is accounted for by the factor γ, which has a value between 0·5 and 1·0. The diffusivity increases with increasing temperature.

Practical values of γD_{gas} that have been found are 0·05–0·1 cm²/sec for nitrogen and carbon dioxide, and 0·20–0·40 cm²/sec for hydrogen and helium as carrier gas (at about atmospheric pressure). If the latter gases are used it is important to operate the column at high gas velocities in order to make the diffusion term as small as possible. Because of the low viscosities of hydrogen and helium, the pressure drop over the length of one theoretical plate is smaller for these gases than for nitrogen and carbon dioxide, although this length may be appreciably smaller with the latter gases.

From the point of view of column efficiency it is not easy to predict which of the carrier gases commonly employed is to be preferred. Anticipating on the subsequent section, we may say that if the mass transfer coefficient C in equation (2) is small we can operate a column efficiently at high gas velocities because the molecular diffusion becomes negligible. In this case the less viscous gases are preferable. If, however, C is comparatively large, either the molecular diffusion term or the mass transfer term is of importance and then it is more efficient to use, say, nitrogen at a relatively low velocity.

3. The term $\frac{8}{\pi^2} \cdot \frac{k'}{(1+k')^2} \cdot \frac{d_f^2}{D_{liq.}} \cdot u$; the resistance to mass transfer

In this term various parameters occur. The effect of k' will be discussed first. The factor $k'/(1+k')^2$ has a maximum value at $k' = 1$, where $k' = KF_{liq.}/F_{gas}$ and K is the partition coefficient*.

Values of K between 10 and 500 are normal in GLPC. The fractional cross sections $F_{liq.}$ and F_{gas} may vary considerably; for columns with 10–40 parts weight of liquid on 100 parts weight of dry packing $F_{liq.}/F_{gas}$ lies between 0·05 and 0·25.

Large values of k' decrease the coefficient C of u in the mass transfer term. Means for decreasing C via k' are therefore:

(*a*) increasing K by lowering the temperature (this will increase the concentration of the solute in the liquid) or by taking another stationary liquid in which the solute is more soluble;

(*b*) increasing $F_{liq.}/F_{gas}$ by increasing the amount of stationary liquid.

Both means, however, affect the other factors in the mass transfer term.

(*i*) A decrease in temperature will increase the viscosity of the stationary

* In vapour–liquid equilibria K is frequently defined as the quotient of the concentration in the gas phase and the concentration in the liquid phase, and then $k' = KF_{gas}/F_{liq.}$; it is immaterial which of the two definitions is used here, because the factor $k'/(1+k')^2$ does not change if k' is replaced by $1/k'$.

liquid and hence decrease the diffusivity $D_{liq.}$ of the solutes in the liquid. Frequently the overall effect will be a decrease in the mass transfer term. Some liquids, however, for instance phthalic esters, tend to form a glass at low temperatures and then $D_{liq.}$ will have quite low values; the mass transfer term then controls the separation under any set of conditions.

(*ii*) An increase of $F_{liq.}/F_{gas}$, though decreasing the factor $k'/(1 + k')^2$ will increase the value of d_f, which occurs as its square. Taking for instance columns with 5, 15, 30 and 45 per cent of hexadecane on 30/50 mesh Sterchamol and *n*-butane ($K \sim 40$ at 30°C) as the solute, the value of $k'd_f^2/(1 + k')^2$ increases in the ratio 0·15, 1·86, 7·31, 12·30 (vide *Table III*).

Only for very low values of K ($KF_{liq.}/F_{gas} \sim 1$) can an increase in the amount of stationary liquid reduce the mass transfer contribution to the HETP. Very low values of K, however, are not feasible; the solute content per plate is very small and effective separations can be attained with extremely small samples only.

Values of the coefficient in the mass transfer term have been seen to depend upon various parameters. In practice the values may vary between 0·001 for 'lean' columns coated with a liquid of low viscosity and high values of K (>100), and 0·1 or more for 'rich' columns with a liquid of high viscosity and low value of K (~10).

Experimental

A few experiments will be described in which the HETP was determined with a variation of certain parameters. In these experiments the following effects have been studied:

1. Variation in the amount of stationary liquid.
   Columns packed with a 30/50 screen fraction of Sterchamol, coated with 5, 15, 30 and 45 parts by weight of hexadecane on 100 parts by weight of support, were employed. The carrier gas was hydrogen.
2. The nature of the carrier gas.
   For the 30/50 mesh Sterchamol and 30 parts hexadecane column hydrogen and nitrogen were used as the carrier gas.
3. Particle size of the carrier.
   With nitrogen as the carrier gas, 30 per cent hexadecane columns with 20/30 and 30/50 screen fractions of Sterchamol have been compared.

Apparatus and Procedure

The apparatus has been described elsewhere[9]; the only modification was that the vapour jacket originally used for temperature control was replaced by an oil thermostat. All experiments were carried out at 30°C in 360-cm coiled copper columns. Measurements were carried out on a standard mixture of propane (2·5 per cent by volume); *iso*butane (92·7 per cent by volume) and *n*-butane (4·8 per cent by volume). The sample charge was always 1 ml.

As the effective number of plates of a GLPC column decreases with increasing concentration of the component, the actual measurements were carried out on propane and *n*-butane, the amounts of which were so small that the number of plates is not yet affected.

The peak widths, p, for *n*-butane and propane were measured from the chart in millimetres. As width of a peak, the base line intercept of the two

Table 1

Hexadecane–Sterchamol 30–50, Hydrogen, 30°C. Column length 360 cm.

Description				1/*h*	p_i mm Hg	p_o mm Hg	*Linear velocity at average col. pres.* cm/sec	*Final retention volume R.V.* mm		*Peak width* mm		*HETP eff.* cm		*Recorder chart speed* cm/h
								C_3	nC_4	C_3	nC_4	C_3	nC_4	
Ratio: support/solvent		100 : 45												
Column volume	100	cm³		1	798·9	765·9	1·65	102·1	300	12·6	30·9	0·406	0·265	30·5
Support volume	17·80	cm³		2	785·4	722·4	3·23	108·1	315·2	12·7	30·7	0·349	0·235	61·0
Liquid volume	22·66	cm³	100	4	787·6	666·6	6·17	57·3	166·4	7·7	18·1	0·460	0·298	61·0
'Free' gas volume	59·54	cm³		6	787·3	613	8·84	40·9	116·8	6·4	14·2	0·649	0·381	61·0
'Free' gas cross section	0·165	cm²		10	798·6	531·6	13·46	26·7	76·2	4·5	10·3	0·800	0·480	61·0
Liquid cross section	0·0629	cm²												
Ratio: support/solvent		100 : 30												
Column volume	102	cm³		1	793·9	767·9	1·43	157·4	426·2	19·2	49·2	0·380	0·337	61·0
Support volume	18·08	cm³		2	782·5	730·5	2·81	78·0	212·0	8·1	20·2	0·257	0·225	61·0
Liquid volume	15·34	cm³	102	3	785·2	711·3	4·15	54·1	146·7	5·2	13·2	0·230	0·187	61·0
'Free' gas volume	68·58	cm³		4	785·3	686·3	5·43	40·6	110·4	4·0	9·3	0·235	0·175	61·0
'Free' gas cross section	0·191	cm²		5	778·8	654·8	6·64	32·8	89·3	3·3	7·9	0·253	0·191	61·0
Liquid cross section	0·0426	cm²		10	785·0	563·0	12·26	18·1	49·9	2·1	5·2	0·325	0·272	61·0
Ratio: support/solvent		100 : 15												
Column volume	105·5	cm³		2	769·0	714·5	2·49	60·1	135·1	6·3	13·7	0·274	0·255	61·0
Support volume	19·72	cm³		4	769·1	661·1	4·78	31·2	70·2	2·7	6·1	0·184	0·186	61·0
Liquid volume	8·37	cm³	105·5	6	788·0	626·0	6·86	106·9	237·8	9·0	20·2	0·174	0·168	305·0
'Free' gas volume	77·41	cm³		10	789·5	541·5	10·51	72·4	158·8	6·3	13·9	0·181	0·182	305·0
'Free' gas cross section	0·215	cm²												
Liquid cross section	0·0233	cm²												
Ratio: support/solvent		100 : 5												
Column volume	95·9	cm³		2	778	726	2·51	191·4	304	19·1	31·4	0·249	0·282	305·0
Support volume	16·94	cm³		4	778·3	679·3	4·86	101·0	159·8	15·4	8·9	0·192	0·231	305·0
Liquid volume	2·40	cm³	95·9	6	783	640	7·04	70·4	110·9	5·9	11·1	0·170	0·250	305·0
'Free' gas volume	76·56	cm³		8	776	558	10·91	46·2	73·0	3·4	7·0	0·127	0·228	305·0
'Free' gas cross section	0·213	cm²												
Liquid cross section	0·0067	cm²												

Table II

Hexadecane-Sterchamol 100–30, Nitrogen, 30°C. Column length 360 cm

Description				1/*h*	p_i mm Hg	p_o mm Hg	*Linear velocity at average col. pres.* cm/sec	*Final retention volume R.V.* mm		*Peak width* mm		*HETP eff.* cm		*Recorder chart speed* cm/h
								C_3	nC_4	C_3	nC_4	C_3	nC_4	
Mesh size support		30–50		0·5	783·4	757·4	0·71	153·6	415·4	13·6	33·9	0·198	0·189	30·5
Column volume	102	cm³												
Support volume	18·08	cm³	} 102	1	779·7	728·7	1·38	158·9	421·2	12·3	30·4	0·145	0·125	61·0
Liquid volume	15·34	cm³												
'Free' gas volume	68·58	cm³												
'Free' gas cross section	0·191	cm²		2	787·4	689·5	2·72	82·4	223·4	6·2	16·9	0·138	0·139	61·0
Liquid cross section	0·0426	cm²												
				5	788·7	572·7	6·12	38·3	102·7	3·6	8·7	0·214	0·187	61·0
Mesh size support		20–30		2	783·2	727·2	2·74	74·9	194.4	7·9	21·6	0·276	0·313	61·0
Column volume	100	cm³												
Support volume	16·09	cm³	} 100	4	785·9	678·9	5·28	40·2	102·9	4·6	13·0	0·299	0·395	61·0
Liquid volume	13·66	cm³												
'Free' gas volume	70·25	cm³												
'Free' gas cross section	0·195	cm²		6	788·6	630·6	7·60	136·5	356	15·3	45·5	0·337	0·429	305·0
Liquid cross section	0·379	cm²												
				10	800·4	557·4	11·70	91·0	236·8	10·4	32·8	0·405	0·506	305·0

inflection tangents was taken. The (corrected) distance, d, between the injection point and the intersection of the second inflection tangent with the base line was also measured in millimetres, and was corrected for the gas hold-up of the column.

The number of plates was calculated from

$$n = \{4(d/p) - 2\}^2 \text{ (see van Deemter } et\ al.^{5})$$

and the HETP from $H = 360/n$ cm.

Table III

Comparison of Data for Columns with Various Amounts of Stationary Liquid

Hexadecane per cent		5	15	30	45
$F_{liq.}$		0·0067	0·0233	0·0426	0·0629
F_{gas}		0·213	0·215	0·191	0·165
k'–C_3		0·36	1·24	2·54	4·34
k'–nC_4		1·2	4·1	8·5	14·5
$k'/(1 + k')^2$–C_3		0·194	0·247	0·203	0·152
$k'/(1 + k')^2$–nC_4		0·248	0·158	0·094	0·060
$k'd_f^2/(1 + k')^2$–C_3		0·19	2·22	7·31	12·30
$k'd_f^2/(1 + k')^2$–nC_4		0·25	1·42	3·38	4·86
Slope of curve as calculated from 45 per cent *column*	C_3	0·0008	0·010	0·033	0·055*
	C_4	0·0015	0·008	0·019	0·028*

* Experimental values

The linear gas velocity, u, was calculated from the measured volume rate at the outlet, corrected for the vapour pressure of water in the wet gas meter and then converted to column temperature (30°C) and the average column pressure. This means that a constant value of u was assumed over the whole column, which seems permissible as $p_i/p_o < 1.5$ in all experiments.

Values of the HETP were plotted against the linear gas velocity. The experimental data are summarized in *Table I* for the experiments in which the amount of stationary liquid was varied and in *Table II* for the variations in particle size and carrier gas.

The values of the partition coefficient, K, for n-butane and propane were calculated from the retention volumes. These values will be required in the discussion of the experiments. They are:

$$\left.\begin{aligned} K_{\text{propane}} &= 11{\cdot}4 \pm 0{\cdot}3 \\ K_{n\text{-butane}} &= 38{\cdot}0 \pm 0{\cdot}3 \end{aligned}\right\} \text{(at 30°C in hexadecane).}$$

Review of Experimental Data

(See *Figures* 5(a)–(d), *6* and *7*).

(*a*) *Variation in the amount of stationary liquid*

The amount of stationary liquid, as discussed, affects the coefficient of the mass transfer term in two ways, viz. by a change in $k' = KF_{liq.}/F_{gas}$; and by a change in the effective liquid film thickness d_f.

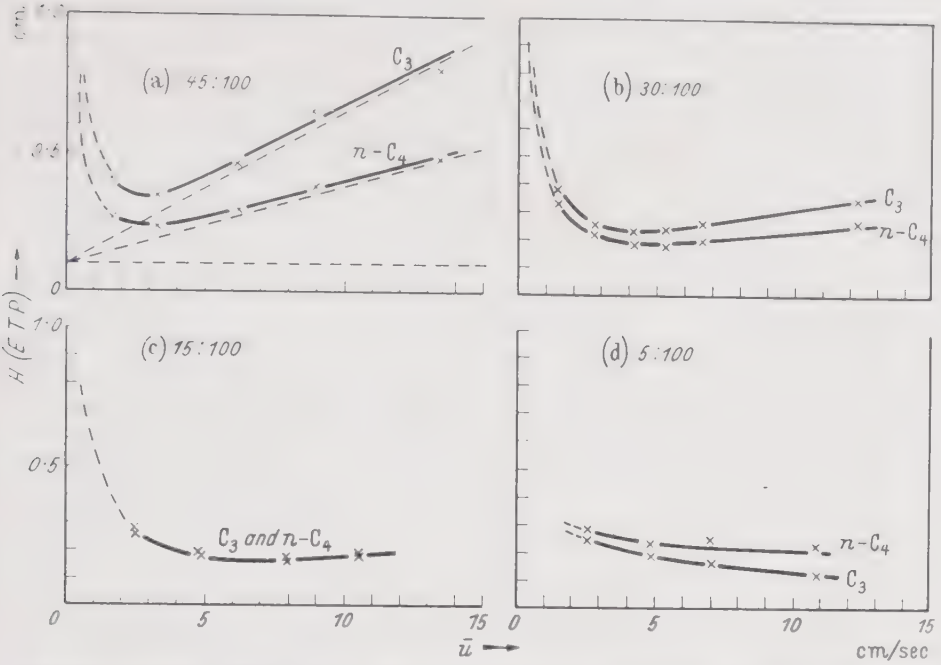

Figure 5. Curves of H against u for various ratios of hexadecane to Sterchamol 30/50: (a) 45 : 100, (b) 30 : 100, (c) 15 : 100, (d) 5 : 100. *Solutes: propane and* n-*butane. Carrier gas: hydrogen*

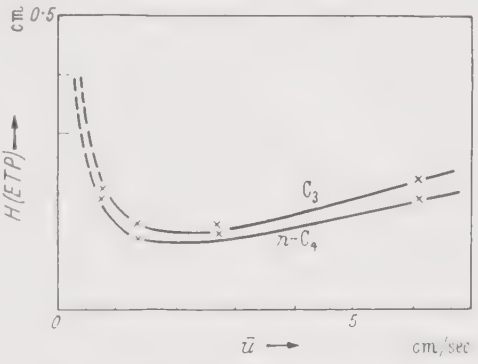

Figure 6. Curves of H against u for 30 : 100 *hexadecane/Sterchamol. Solutes: propane and* n-*butane. Carrier gas: nitrogen; support* 30/50 *mesh*

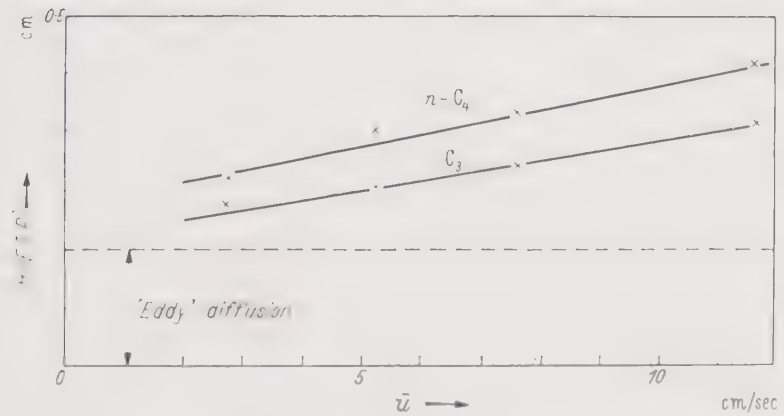

Figure 7. As Figure 6, but support 20/30 *mesh*

The values of k' could be calculated from K and the column data.

The effective film thickness is not easy to estimate, but if we arbitrarily assign the value of 1 to the thickness of the film in the 5 per cent column, that in the 15, 30 and 45 per cent columns will be less than 3, 6 and 9 respectively and hence d_f^2 will increase less than in proportion to 1 : 9 : 36 : 81, which values have been taken in the evaluation of the relative experiments. In this way the ratio of the coefficients of the mass transfer term for the various columns could be estimated.

This coefficient was determined from the curve corresponding to the 45 per cent column and was found to be 0·055 sec for propane and 0·028 sec for *n*-butane, the ratio being 2, whereas theory would predict a ratio of about 2·5.

The slope of the other curves was calculated from those of the 45 per cent column, taking into account the decrease in d_f and the decrease in $F_{liq.}/F_{gas}$. These calculated data are given in the last two lines of *Table III*. At 15 per cent the curves will tend to coincide, a deduction which is in fair agreement with the experiments, whilst for the 5 per cent column the slope of the butane curve becomes even larger than that for propane.

In view of the low values of the coefficients in the mass transfer term these experiments are not suitable for providing a more quantitative test of the theory. Moreover, we do not believe that more than a qualitative description of the phenomena may be expected, in view of the assumptions made in the derivation of van Deemter's equation.

(*b*) *The coefficient of the diffusion term*

The coefficient of the diffusion term $\gamma' D_{gas}$ for nitrogen and hydrogen may be estimated from the relative curves with the 30 per cent hexadecane column. This estimate again can only be very rough.

For hydrogen the HETP at $u = 1{\cdot}45$ cm/sec is 0·38 cm (propane).

For nitrogen the HETP at $u = 0{\cdot}75$ cm/sec is 0·20 cm (propane).

In the formula $H = A + B/u + Cu$, $C = 0{\cdot}033$ cm²/sec (*Table III*). $A = 0{\cdot}1$ cm seems to be a good estimate for the eddy diffusion. For the value of $B\ (= \gamma' D_{gas})$ we then find 0·33 cm²/sec for hydrogen and 0·06 cm²/sec for nitrogen.

(*c*) *The constant A*

Whilst 0·1 cm has appeared to be a good estimate for A with 30/50 screen fractions, this value increases to about 0·2 cm for the 20/30 fraction.

20/30 fraction	$2\lambda d_p \sim 0{\cdot}2$ cm	$d_p \sim 700\mu$	$\lambda \sim 1{\cdot}4$
30/50 fraction	$2\lambda d_p \sim 0{\cdot}1$ cm	$d_p \sim 440\mu$	$\lambda \sim 1{\cdot}2$

The values of λ for these packings are about equal, so that the value of A is largely determined by the particle diameter d_p.

Conclusions

If, for a difficult separation, it is necessary to construct a column with a large number of plate equivalents, and to operate such a column under the most favourable conditions, the following points should be taken into account.

(*1*) Attention should be given to an efficient column packing. Although it might appear at first sight that very fine particles are the most favourable, it

is not easy to pack such a support with sufficient regularity. Experimentally it has been found that a narrow screen fraction between 30 and 80 mesh ASTM (between 590 and 177μ diameter) will give a contribution of about 0·1 cm to the HETP independent of the operating conditions.

(*2*) Although the gas velocity increases from column inlet to column outlet it is possible to choose the outlet gas velocity in such a way that the average HETP is hardly more than the minimum HETP attainable.

When using a high ratio of inlet to outlet pressure particular care should be taken that the gas velocity is not so low that the column is operating in the region where molecular diffusion badly impairs the HETP (see *Figure 2*).

(*3*) Better separations are generally obtained at lower column temperatures. It should, however, be realized that the diffusivity of the stationary liquid decreases at the same time, so that it is not possible to take full advantage of the increase in K. It may occur that the diffusivity of the liquid becomes so low that this factor practically controls the HETP.

(*4*) The amount of stationary liquid on the support should not be too high. On the other hand with very low amounts of stationary liquid the sample that can be introduced is extremely small. Furthermore, the packing is then frequently not sufficiently inert so that it exhibits adsorptive capacities towards the solutes. 15–20 per cent of solvent is usually a good compromise.

(*5*) Very high efficiencies are more easily attainable with nitrogen than with hydrogen or helium.

The construction of a 20-metre column, having an average HETP of 2 mm, and thus giving 10,000 theoretical plates, seems quite feasible. With such a column it might be possible to separate solutes with relative volatilities of only 1·05, for instance meta- and para-xylene.

The authors thank the management of the Koninklijke/Shell-Laboratorium, Amsterdam, for permission to communicate the contents of this paper.

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DISCUSSION

E. Glueckauf: It is generally assumed and has been re-stated by Keulemans and Kwantes that the eddy diffusion term, and in particular the factor λ, is characteristic of column packing and does not depend on operating conditions (e.g. flow rate). In order to test this we did experiments with non-adsorbing glass beads in columns and observed the spread of a point source of radioactive tracer (HI)* which was washed through the columns with acidified water. Under these conditions the

spread is entirely due to the eddy diffusion term which consequently can be assessed accurately. We found in these experiments that the ratio of HETP to particle diameter varied markedly with the flow rate (see *Figure 8*) and the curves obtained varied only moderately with the size and method of packing. With this liquid–solid system, values of λ varying between 0·5–3 were obtained, the larger of which agrees with the observations by Klinkenberg and Sjenitzer for gas–solid systems.

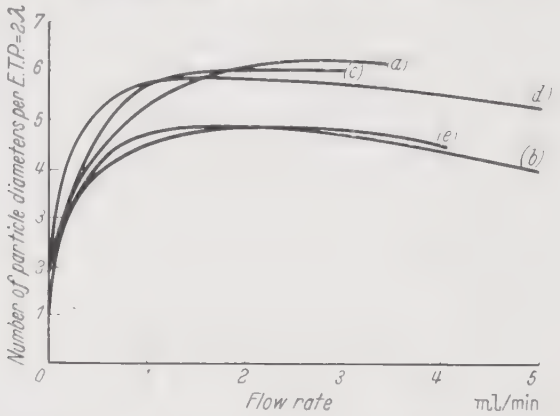

Figure 8. Ratio of HETP to particle diameter as a function of flow rate. Column 40 cm *long, internal diameter* 1·0 cm, *filled with: (a) thick slurry of* 60/70 *screened Ballotini, without tapping; (b) as (a) but with tapping; (c) thick slurry of* 60/90 *screened Ballotini, without tapping; (d) thin slurry as (c) but with tapping; (e) thick slurry of* 30/36 *screened Ballotini, without tapping*

E. F. G. HERINGTON: Referring to the last paragraph of Keulemans and Kwantes' paper I would like to discuss the behaviour of a large number of theoretical plates in chromatographic and distillation experiments. It occurred to me that there may be people who have worked on distillation and who may be impressed by the thousands of theoretical plates used in chromatography. However, calculation indicates that in general fewer plates are required in distillation than in chromatography to achieve the same separation. For example, if n theoretical plates are required in distillation to obtain a given separation, then approximately n^2 plates may be required in chromatography.

To quote a specific example 580 theoretical plates are required in a distillation column to prepare a sample of 99·9 per cent purity from a 50 : 50 binary mixture of relative volatility ratio 1·012 but 500,000 theoretical plates are required in a chromatograph column. The reason for this difference is that, in a sense, plates are used over and over again in a distillation column whereas they are used only once in a chromatograph column.

I am aware of the great advantages of using gas–liquid chromatography for many purposes (e.g. in analysis) and I merely wish to emphasize here that the transference of the theoretical plate concept from distillation to gas–liquid chromatography may be misleading if the different way in which theoretical plates are used in these techniques is not appreciated.

A. I. M. KEULEMANS: I fully agree with Dr Herington's observation that the number of plate equivalents required for a separation by chromatography is much larger than the number of plate equivalents for the same separation in a countercurrent process such as distillation. However, apart from other advantages of the chromatographic techniques, the high number of plates required in chromatography is often easier to realize in a laboratory than the corresponding lower number of plates in distillation or extractive distillation.

When comparing separation processes, particularly chromatographic processes, in which a fixed phase is involved, with countercurrent processes, in which there are two moving phases, the plate concept may give rise to some confusion.

An example will be discussed that may shed some light upon this problem. Following a suggestion by Dr Martin we will consider a column which is bent in a circle, the exit running into the inlet. If in such a column an infinitely narrow band of solute is introduced and circulation of carrier gas is set up, the solute band will move round the column and arrive after a certain time at its point of introduction as a band of certain width. If p is the number of plate equivalents of the column the width at half height will be $2p^{\frac{1}{2}}$. When the band arrives a second time at its point of introduction the width will be $2(2p)^{\frac{1}{2}}$, until after p revolutions the width at half

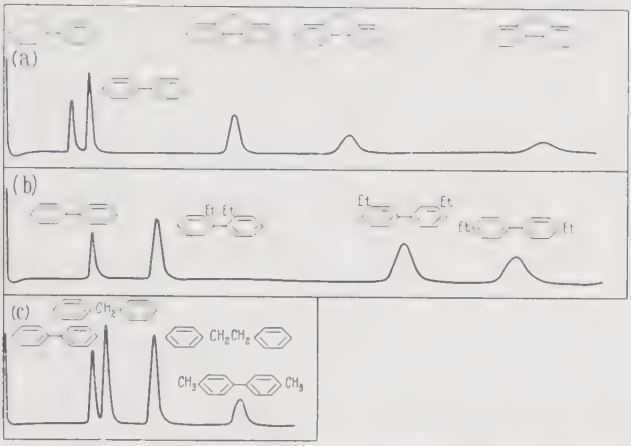

Figure 9. Vapour-phase chromatograms of alkyldiphenyls and related compounds. Stationary phase, Apiezon M on kieselguhr; temperature 198° C; *carrier gas, nitrogen at* 75 cm Hg. *Compounds shown, reading from left to right:* (a) *Diphenyl, fluorene,* 9:10-*dihydrophenanthrene, phenanthrene* (*Total sample volume* 0·42 μl); (b) *Diphenyl,* 2:2′-*diethyldiphenyl,* 3:3′-*diethyldiphenyl,* 4:4′-*diethyldiphenyl* (*Total sample volume* 0·61 μl); (c) *Diphenyl, diphenylmethane, dibenzyl,* 4:4′-*dimethyldiphenyl* (*Total sample volume* 0·61 μl). *Retention volumes increasing from left to right*

height is $2p$ and the solute is almost homogeneously distributed over the whole column. From that time on further circulation will not bring about any change and the situation may be compared to that of the steady state in a countercurrent process. Although the column was equivalent to p equilibration steps only, the steady state was arrived at after p^2 of such steps. In passing it may be noted that the time required for getting a distillation column under total reflux is roughly proportional to the square of its number of plate equivalents.

G. H. Beaven: In the course of work carried out in conjunction with Drs A. T. James and E. A. Johnson, the behaviour of a number of compounds related to diphenyl has been investigated on columns of Apiezon M on kieselguhr at 200° C. It appears that the retention volumes of these compounds, relative to diphenyl itself, are very sensitive to steric effects, i.e. to the operation of structural features which control the extent to which coplanarity of the two benzene rings can be approached.

Steric effects of this kind are known to produce considerable and characteristic changes in the ultraviolet absorption spectra of these compounds. These are most prominent when substitution occurs in two or more of the *ortho* (i.e. 2- and 6-) positions, since the extent of diphenyl-type conjugation depends on the angle between the benzene ring planes. *Figure* 9(b) shows the corresponding chromatographic effects for the three isomeric symmetrical diethyldiphenyls, using diphenyl

as a marker. For the 4:4′- isomer the factor (n) for the increase in retention volume per additional $-CH_2-$ is 1·55, which is almost identical with the value for an aliphatic $-CH_2-$ group*, while the severely hindered 2:2′-isomer has a greatly reduced retention volume ($n = 1{\cdot}15$).

In *Figure* 9(c) a similar comparison may be made between the conjugated 4:4′-dimethyldiphenyl ($n = 1{\cdot}62$) and the essentially unconjugated and flexible molecule of dibenzyl ($n = 1{\cdot}30$). In diphenylmethane the introduction of a single carbon atom between the two benzene rings breaks the conjugation and results in a retention volume scarcely greater than that of diphenyl, and much less than would be expected for 4-methyldiphenyl.

Figure 9(a) shows some effects of bridging in the 2:2′-positions and especially of additional conjugation. It has been shown* that alicyclic hydrocarbons have a higher retention volume than their straight-chain analogues, and both fluorene and 9:10-dihydrophenanthrene have greatly increased retention volumes when compared with 2-methyl- and 2-ethyl-diphenyls respectively, but in this group of compounds increased conjugation in planar or near-planar structures also plays a significant part.

Many other substituted diphenyls have also been investigated and close parallels between chromatographic and spectroscopic evidence for these steric effects have been observed throughout. This work is being published in detail elsewhere.

C. L. Dunn: I would like to ask the last speaker whether he attributes this difference in the various ethyl derivatives to the vapour activity coefficient or vapour pressure difference, or whether he has any idea which factor is accounting for this.

G. H. Beaven: Not the slightest, I am afraid.

A. Klinkenberg: Dr Herington in comparing, in his discussion of the above paper, gas–liquid partition chromatography to countercurrent distillation, mentioned the possibility of the variation of the nature of the stationary phase as a specific advantage of the former.

A similar effect, however, is also reached in extractive distillation. The normal aliphatic alcohols, for instance, in the presence of a generous amount of water are more volatile, the higher the carbon number, i.e. the effect of chain length on boiling point is over-compensated by its effect on activity coefficient.

A. J. P. Martin: Will Dr Herington amplify his comparison of distillation and chromatography.

In chromatography many of the bands separated have purities much higher than those quoted in the overall separation. I fancy in the example quoted by Dr Herington his purity refers to the best sample producible. What proportion in his example is available in the purity he gives?

E. F. G. Herington: Comparison of distillation with chromatography is difficult because these techniques are usually employed for entirely different purposes. However, the data quoted earlier refer to the following hypothetical experiments. Suppose that a 0·5 ml specimen of 99·9 per cent purity is to be prepared from a litre of a 50 : 50 binary mixture containing components with a relative volatility ratio 1·012. Then the preparation might be carried out as follows:

Distillation

A column fitted at the top with a small reservoir of 0·5 ml capacity which can be flushed with the condensate is erected. The litre of mixture is put in the boiler and the column run under total reflux until a stationary state is reached. The purified sample of more volatile component can then be withdrawn. The Fenske equation

$$n = \{\log [y/(1 - y)] - \log [x/(1 - x)]\} / \log \alpha$$

* James, A. T. and Martin, A. J. P., *J. appl. Chem.* **6**, 105, 1956.

can be used to calculate the number of plates required. In this way n is found to be 580 when $y = 0{\cdot}999$ and $\alpha = 0{\cdot}4995$.

Gas–liquid chromatography

1 ml of the 50 : 50 mixture is put on the column and 0·5 ml of product collected. The number of theoretical plates required to produce a material of 99·9 per cent purity can be obtained by extrapolation of the graph due to Glueckauf (see *Figure 3* of *Trans. Faraday Soc.* **51**, 34, 1955). An approximate value of 5×10^5 is so obtained.

It is, of course, possible to stipulate other conditions for carrying out the separation and then different values for the number of plates required will be found but my main thesis is that a worker on distillation need not be too overawed when he sees references to chromatograph columns containing 10,000 theoretical plates.

E. Glueckauf: I think the real crux of the matter in a comparison between chromatography in any sense and distillation or other continuous process is the quantities involved. One really cannot set up a distillation process when one is dealing with milligrammes and other quantities which are of interest for analytical purposes. But when it becomes a question of production, then quite clearly any continuous process like distillation is far superior to anything which can be done with a column, and I think everyone would agree with this.

On the question which was raised by Dr Martin about the system of a very large column, we have quite a lot of experience in this field from distillation columns used for the separation of isotopes. We have a system, for instance, that has 500 theoretical plates in it, and used in the proper distillation manner we have separation factors of the order of 1·005. Under these conditions one can, of course, separate substances with a purity which is acceptable by calculation in a straightforward manner. It depends on the separation factor. But the difficulty of running a distillation column, which is not normally appreciated, lies in the very long equilibrium time which such a column requires. It is something of the order of a fortnight to a month before the product appears with its appropriate purity on the top of the column.

Another difficulty which arises in this case, which one does not have with chromatographic separations, is that if one distils substances which are very difficult to separate, then the upflow—the boil-up rate as it is usually called—has to be very small even if the column is run on total reflux. This means that the temperature all along the very long column has to be controlled with special care, and there is no question at all about it that chromatographic separations, even on a 10,000 plate column, are very much easier to carry out than distillation, even on a column which contains only 100 plates.

R. W. P. Scott: I would like to say that in our laboratories we have done quite a lot of work on similar lines to that done by Dr Kuelemans. I feel there are one or two points that are worth noting. The first is that Dr Kuelemans states that roughly between 15 and 23 per cent of the liquid phase operates with optimum efficiency. We have found also that 18 per cent of liquid phase gives an optimum efficiency. When greases and waxes such as silicone grease and carbowax are employed, however, the optimum value falls to 8–10 per cent.

I also agree that an optimum flow rate exists for the maximum efficiency. In support of the molecular diffusion effect described by Dr Kuelemans, if you confine your interest to the peak width at gas flow rates below the optimum and plot the width against time, you get a straight line. For a series of homologous hydrocarbons such as *n*-paraffins you get a series of straight lines the slopes of which are in proportion to the molecular weights. With a single hydrocarbon at a series of temperatures you will find that the slope approximately relates to the square root of the absolute temperature, which again supports this theory of molecular diffusion.

C. L. DUNN: As I reflect back to the remarks made regarding comparison of distillation and GLPC, I fear some people may carry away a misconception from this meeting. We must not forget that in GLPC we are dealing with the very effective use of selective solvents, and that by all means GLPC does a great deal more than we can hope to achieve in normal distillation. In a great many cases extractive distillation comes in here, but the use of that, particularly on a small scale, is a troublesome job, to say the least. I think the comparison wants to be made with a great deal of caution.

4

THE CONCENTRATION FACTOR IN VAPOUR PHASE PARTITION CHROMATOGRAPHY

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Unsymmetrical peaks in vapour phase partition chromatography need not be due to non-linear partition. With propylene or propane as solute and tri*iso*butene as solvent on Celite, the isotherms are linear but the peaks are unsymmetrical. Using the method of frontal analysis with nitrogen or hydrogen as carrier gas, the transition region both for saturation and elution is found to be proportional to the time the region is on the column. The proportionality constant varies with solute concentration and only at zero concentration is a completely symmetrical peak possible. There is also strong dependence on carrier gas, e.g. with hydrogen instead of nitrogen, although sensitivity is increased the spread is greater and peak overlap occurs.

A dynamical diffusion model has been developed showing that the transition region tends to lengthen at a finite and almost constant rate as the solute concentration is decreased and to shorten (ultimately to a discontinuity) as the concentration is increased. The theory is extended to cover the case of peak overlap.

Part I. Experimental

It is usually considered, following Martin and Synge[1] that the vapour phase partition chromatogram is symmetrical when the partition coefficient of the solute in the column liquid is independent of solute concentration. Asymmetry is attributed to a non-linear isotherm, as, for example, when the column is supposedly overloaded[2]. Keulemans, Kwantes and Zaal[3] also deduce that the chromatogram should be symmetrical, approximating to a gaussian or normal error curve. The present study of the behaviour of propylene and propane on a column with tri*iso*butene as stationary phase shows that asymmetry can still be marked despite linear isotherms and that the degree of asymmetry depends both on solute concentration and on the nature of the carrier gas, but is independent of column temperature and carrier gas rate.

Experimental

The isotherms and the shape of the chromatograms were investigated by frontal analysis. In this method mixtures of various concentrations of the solute (i.e. propane or propylene) and carrier gas are made up and used to saturate the column. The column is then eluted with a stream of carrier gas and the times for saturation and elution measured. From these times the solubility of the solute in the column liquid is calculated and, from the length of the transition regions between gas mixture and carrier gas, information about the spread of the chromatogram is obtained.

A block diagram of the apparatus is shown in *Figure 1*. The carrier gas was taken from a cylinder and its flow rate determined with an aniline flowmeter. The gas mixtures were made up in a 20 litre aspirator and displaced by water at constant rate. Both mixture and carrier gas were luted in the same lute and an identical capillary to that in the aniline flowmeter was placed in the gas mixture line to give the same inlet pressure to the column. Tests showed that the viscosities of mixtures containing low concentrations of propane and propylene in nitrogen did not vary significantly from that of nitrogen alone. All gases and gas mixtures were dried by passing through calcium chloride drying tubes before passing on to the column.

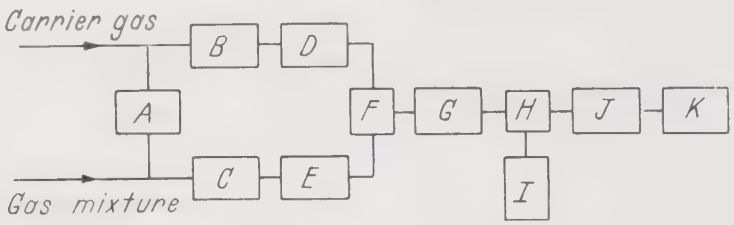

Figure 1. Block diagram of apparatus

A, Water lute; B, Aniline flowmeter; C, Flowmeter capillary; D, E, Drying tubes; F, H, Two-way taps; G, Chromatograph column; I, Mercury manometer; J, Katharometer; K, Manostat and vacuum pump

The column was 150 cm of $\frac{1}{4}$ inch Pyrex tubing completely enclosed in a lagged outer tube. A suitable thermostatting fluid was circulated through the annulus between the two tubes. The tube packing was 19·6 g of a mixture of 30 g of tri*iso*butene (boiling range 189–194 °C) and 70 g of Celite 535 from which the 'fines' had been removed. (The 'fines' were the smaller particles of Celite which did not settle in water in 3 minutes.) A mercury manometer could be connected to the exit end of the column to measure the exit pressures. The gas emerging from the column passed through a thermal conductivity cell and the concentration of solute was recorded on a Sunvic recording potentiometer having a full scale deflection of 15 mV and a chart speed of 3 inches per minute. A manostat and vacuum pump were used to control the exit pressure and thereby the flow rate. The 'dead-spaces' in the system were kept to a minimum and their volume was measured. Unnecessarily large 'dead-spaces' would have resulted in diffusion of the fronts outside the column.

The solubility of propane in tri*iso*butene was also determined by conventional means using bulk liquid and a propane partial pressure of one atmosphere. The results obtained in this way were compared with those obtained on the column.

The gas space or volume of the mobile phase in the column was determined by connecting the column to a graduated external volume and measuring the change in total volume for known changes of pressure. This was later checked by measuring the time required for the passage of a 'slug' of a very slightly soluble gas, such as hydrogen, through the column at known nitrogen gas rates.

Results

Typical records of saturation and elution runs are shown in *Figures 2*(a) and 2(b). The flow rate was first set by fixing the outlet pressure with carrier gas

passing through the column. At t_0 [*Figure 2*(a), saturation] the gas mixture was allowed to pass on to the column to commence saturation. t_{10}, t_{50} and t_{90} are the times at which the concentrations of the solute in the gas emerging from the column are 10, 50 and 90 per cent of the original concentration passed on to the column. At t'_0 [*Figure 2*(b) elution] carrier gas alone started to pass through the column; t'_{10}, t'_{50} and t'_{90} have the same significance as t_{10}, t_{50} and t_{90} in *Figure 2*(a).

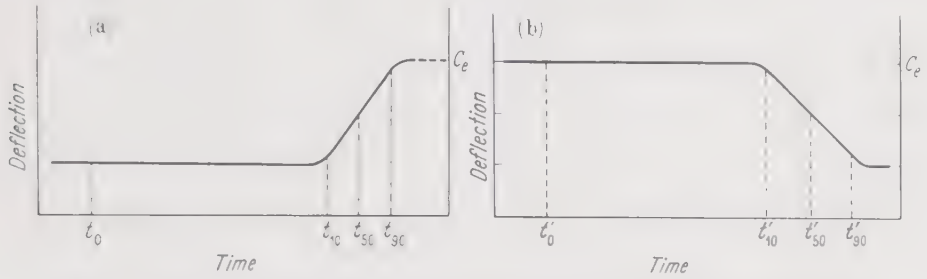

Figure 2. Typical saturation and elution curves showing deflection against time

(i) *Determination of solubility isotherms*—The relationship between the transit time of the carrier gas T_c and the transit time of the solute front T_s may be shown very simply to be

$$T_c/T_s = m/(m + a)$$

where m is the ratio of the volume of the mobile gas phase to that of the stationary liquid phase in the column and a is the solubility coefficient of the solute in the column liquid. As the transition region from carrier gas to gas mixture or vice versa is diffuse the transit time of the solute gas is taken to be t_{50}, the symmetry of the transition region justifying this. It is necessary to correct the value of t_{50} obtained from the recorder chart for the dead-space in the system and also to allow for the change of volume flow brought about by solution and elution on the column. The transit time of the carrier gas is calculated from the gas rate and the volume of the free space in the column. For compressible flow a correction has to be made and the effective volume of the column is given by

$$\frac{\text{Effective volume}}{\text{Actual volume}} = \frac{2}{3}\frac{[1 - (p_o/p_i)^3]}{[1 - (p_o/p_i)^2]}$$

where p_o and p_i are the outlet and inlet pressures respectively (Martin and James[4]).

The solubility coefficient a was calculated for propane and propylene at 20, 0 and −20° C at concentrations of 3, 5, 7 and 9 per cent in nitrogen. These concentrations corresponded to partial pressures up to 70 mm of mercury. Several runs were made at different carrier gas rates and values for $m/(m + a)$ obtained for both saturation and elution runs. A typical series is shown in *Table I*.

The average value for $m/(m + a)$ in column (*3*) is 0·208 and in column (*4*) 0·207. There is therefore no significant difference in the values obtained from saturation runs and elution runs and also no significant variation for $m/(m + a)$ with concentration can be observed.

Table I. Propane in Nitrogen at 0°C

Propane concn per cent (*1*)	*Inlet flow rate* l./h (*2*)	$m/(m + a)$ *Saturation* (*3*)	$m/(m + a)$ *Elution* (*4*)
3	3·80	0·200	0·199
3	2·85	0·205	0·201
3	1·90	0·211	0·208
3	0·95	0·214	0·212
5	3·80	0·205	0·205
5	2·85	0·209	0·207
5	1·90	0·212	2·210
5	1·00	0·207	0·205
7	3·80	0·206	0·205
7	2·75	0·205	0·204
7	1·90	0·211	0·209
7	1·00	0·208	0·207
9	3·80	0·199	0·199
9	2·85	0·213	0·212
9	1·90	0·211	0·206
9	1·00	0·215	0·210

The value of m was calculated from the experimentally determined volume of the gas space in the column and the weight of tri*iso*butene (density known) used in the packing. This was found to be 5·52 at 0°C and, by substitution of this value for m in the mean value for $m/(m + a)$, a could be calculated. The solubility coefficient was found to be 21·15 which is close to the value of 21·3 at 1 atmosphere determined by conventional methods on the bulk liquid.

From the variation of a with temperature the heats of solution of propane and propylene in tri*iso*butene were determined at 10 and −10°C and compared with the heat of vaporization at the same temperatures. These values are shown in *Table II*.

Table II. Properties of Propane and Propylene

Item		*Propane*		*Propylene*	
Temperature	°C	+10	−10	+10	−10
Heat of solution	kcal/mole	3·7	4·0	3·1	3·6
Heat of vaporization	kcal/mole	3·8	4·05	3·2	3·65

The heats of vaporization were taken[5] from *A.P.I. Project 44*.

(ii) *Effect of concentration on length of transition region*—The total length of the transition region was difficult to measure and the quantity used to relate the length of this region to the other factors involved was $(t_{90} - t_{10})$. To eliminate slight irregularities in the trace of the recording instrument, 'deflection' was plotted against time on arithmetical probability paper. A straight line was then obtained and all values of $(t_{90} - t_{10})$ were evaluated in this way.

It was observed that a linear relationship existed between t_{50} and $(t_{90} - t_{10})$ for any one concentration of a solute in the carrier gas, i.e.

$$(t_{90} - t_{10})/t_{50} = \text{constant}$$

This constant did not vary with temperature over the range covered and was unaffected by carrier gas rate. The proportionality constant was, however, always greater for elution than for saturation. *Figure 3* shows the relation

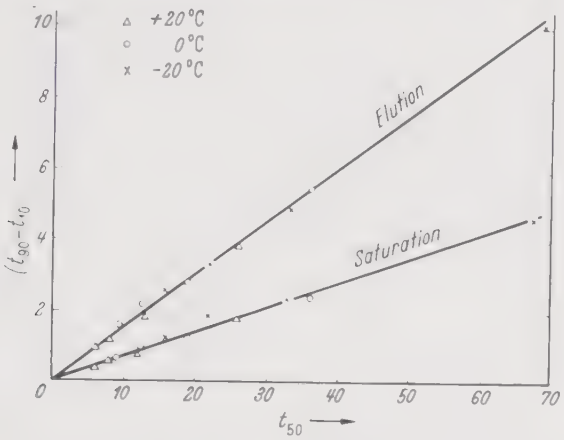

Figure 3. Relation between $(t_{90} - t_{10})$ and t_{50} for a 5 per cent *mixture of propane in nitrogen*

between t_{50} and $(t_{90} - t_{10})$ for a 5% v/v mixture of propane in nitrogen for saturation and elution. The different temperatures are marked and at each temperature the rate was varied between 1 and 4 l./h.

The proportionality constants for propane and propylene in nitrogen at concentrations up to 9% v/v are given in *Table III.*

Table III. Values of $(t_{90} - t_{10})/t_{50}$

Concn / *Solute*	3% v/v		5% v/v		7% v/v		9% v/v	
	Sat.	*Elut.*	*Sat.*	*Elut.*	*Sat.*	*Elut.*	*Sat.*	*Elut.*
Propane	0·081	0·125	0·070	0·148	0·061	0·165	0·054	0·184
Propylene	0·085	0·129	0·076	0·144	0·064	0·161	0·057	0·178

The values of $(t_{90} - t_{10})/t_{50}$ for propane and propylene are not very different. The concentration range was extended to 30 per cent for propane/nitrogen mixtures and a similar series was carried out using up to 20 per cent propane in hydrogen. These results are summarized in *Figure 4* where $(t_{90} - t_{10})/t_{50}$ is plotted against propane concentration for both carrier gases. With the existing apparatus it would be difficult to extend the work to concentrations much below 3 per cent but the extrapolation to zero concentration appears reasonable.

At zero concentration the values of $(t_{90} \quad t_{10})/t_{50}$ for saturation and elution with a given carrier gas coincide but are greater for hydrogen than for nitrogen as carrier gas.

Review

The good agreement obtained between the solubility coefficients determined on the column up to 0·09 atmospheres and in the bulk liquid at 1 atmosphere show that the solubility isotherm is linear throughout the range and that Henry's law applies. This is confirmed by the agreement between the calculated heats of solution on the column and the published heats of vaporization, suggesting that the solution is practically ideal and the heat of mixing negligible. The saturation and elution behaviour is, however, far from symmetrical and asymmetry increases with increasing concentration. The reason for this will be dealt with in the second part of this paper.

Two points of practical interest emerge from this work which are relevant to separation requirements.

(*a*) The relative rates of travel through the chromatograph column of two solutes having partition coefficients a_1 and a_2 are R_1 and R_2 where $R_1/R_2 = (m + a_2)/(m + a_1)$. If a_1 and a_2 are, for example, 5 and 4 respectively and m is 5, $R_1 : R_2 :: 9 : 10$, i.e. $R_1 : R_2 :: 1 : 1{\cdot}11$. If the temperature is then decreased until a_1 and a_2 are 40 and 32 (a_1/a_2 remaining constant), $R_1 : R_2 :: 37 : 45$, i.e. $R_1 : R_2 :: 1 : 1{\cdot}22$ and the separation of the chromatograms should be increased. The chromatograms will, however, take longer to emerge from the column and will be appreciably broader unless the carrier gas rate is increased sufficiently at the lower temperature to maintain a constant residence time. If this is done the separation should be greatly improved.

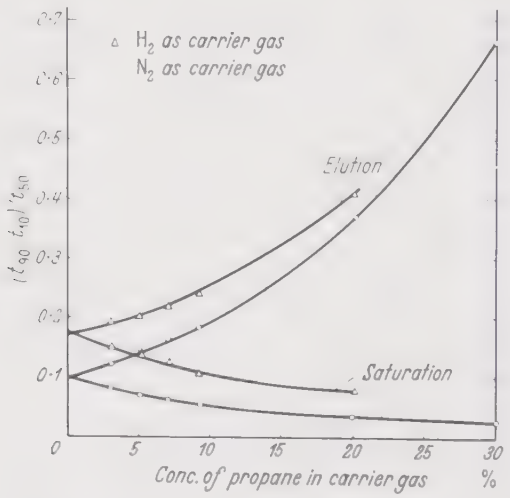

Figure 4. Relation between $(t_{90}-t_{10})/t_{50}$ and propane concentration

(*b*) From *Figure 4* it can be seen that at all concentrations the spread of the chromatogram with hydrogen as the carrier gas is greater than with nitrogen. The separations obtainable with hydrogen should therefore be inferior to those obtainable with nitrogen. *Figure 5* illustrates this with propane and

propylene as the two solutes, tri*iso*butene as the column liquid and nitrogen and hydrogen as carrier gases. As the sensitivity with hydrogen as carrier gas is very high the katharometer current was reduced but all other conditions were kept constant. The difference in peak widths and in the degree of separation obtained is quite marked. The use of hydrogen as carrier gas, although very useful for detecting low concentrations of impurity does, however, reduce the degree of separation obtainable, by increasing the tendency for the chromatograms to overlap.

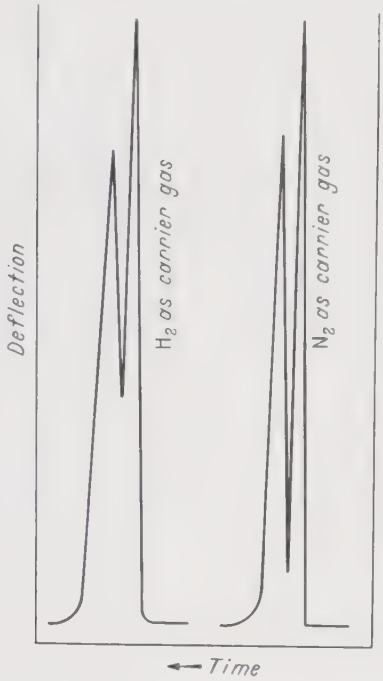

Figure 5. Traces of actual separations of propane and propylene obtained using nitrogen and hydrogen as carrier gases

Part II. Theoretical

An approximately quantitative analysis is given of the flow and diffusion of a gas mixture in a tube with an absorbent packing when the concentrations of the soluble components of the mixture are not very small.

The first case dealt with is the replacement of a pure insoluble gas by a mixture containing a few per cent of a soluble component or vice versa. For brevity the components will be referred to as 'carrier' and 'vapour' respectively.

If t_p is the time elapsed before p per cent of a composition change appears at the tube exit then the 'softening' of the transition region is defined by the ratio $S = (t_{90} - t_{10})/t_{50}$.

It is found experimentally that S is almost independent of gas rate at least over a range of 4 : 1 so that molecular diffusion and time lag in attaining local equilibrium can have no important influence.

S is greater when the carrier is hydrogen than when it is nitrogen so that diffusion may not be quite negligible.

For any one tube and packing let the ratio of dissolved vapour to that in the vapour phase be σ when equilibrium is established; it has been found experimentally that for the vapour used σ is independent of concentration.

Let the concentration of vapour in the mixture be c_1 and while the transition region is wholly within the tube let the mean flow velocity in the interstices of the packing be u_1 at the mixture end and u_0 at the carrier end. On one side of the transition region the total quantity of vapour present per unit volume of free space is $c_1(1 + \sigma)$ and on the other side zero. Clearly the rate of advance of the median point of the transition region must be $u_1/(1 + \sigma)$.

If local equilibrium is attained instantaneously then in any section of the tube a fraction $1/(1 + \sigma)$ of the vapour present is in the vapour phase, the remainder is absorbed in the packing. During saturation vapour is entering at a rate u_1c_1 so that it is being removed from the vapour phase at a rate $u_1c_1 \cdot \sigma/(1 + \sigma)$. This gives

$$u_0 = u_1[1 - \sigma c_1/(1 + \sigma)]$$

This is also correct for elution. In the transition region itself diffusion is important. Molecular diffusion is assumed negligible but an analogous effect is produced by the splitting and recombination of gas streams flowing with different velocities through different sized passages in the packing. This dynamical diffusion obeys similar equations to molecular diffusion but the coefficient is proportional to the flow velocity. Let $D = \Delta u$.

Transport rate of vapour across any cross section is

$$u(c - \Delta \, \mathrm{d}c/\mathrm{d}x)$$

so that

$$u_0 = u\left\{1 - \frac{\sigma}{1 + \sigma}\left(c - \Delta \frac{\mathrm{d}c}{\mathrm{d}x}\right)\right\}$$

and

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\frac{1}{1 + \sigma} \cdot \frac{\mathrm{d}}{\mathrm{d}x}\left\{u\left(c - \Delta \frac{\mathrm{d}c}{\mathrm{d}x}\right)\right\}$$

A more convenient variable than t is X, the distance the median point, or for all practical purposes the 50 per cent point, has travelled from the entrance; thus

$$X = u_1 t/(1 + \sigma)$$

and

$$\frac{\mathrm{d}c}{\mathrm{d}X} = -\left(1 - \frac{\sigma}{1 + \sigma} c_1\right) \frac{\mathrm{d}}{\mathrm{d}x}\left\{\frac{c - \Delta \dfrac{\mathrm{d}c}{\mathrm{d}x}}{1 - \dfrac{\sigma}{1 + \sigma}\left(c - \Delta \dfrac{\mathrm{d}c}{\mathrm{d}x}\right)}\right\}$$

$$- \frac{1 - \dfrac{\sigma}{1 + \sigma} c_1}{\left\{1 - \dfrac{\sigma}{1 + \sigma}\left(c - \Delta \dfrac{\mathrm{d}c}{\mathrm{d}x}\right)\right\}^2} \frac{\mathrm{d}}{\mathrm{d}x}\left(c - \Delta \frac{\mathrm{d}c}{\mathrm{d}x}\right)$$

If c is everywhere small this reduces to

$$\frac{\mathrm{d}c}{\mathrm{d}X} = -\frac{\mathrm{d}c}{\mathrm{d}x} + \Delta \frac{\mathrm{d}^2c}{\mathrm{d}x^2}$$

σ has apparently disappeared from this formula but it is not *a priori* obvious whether Δ is dependent on σ or not.

Imagine two tubes with packings geometrically identical but with different values of σ. Let the flow rates in the tubes be in the same ratio as the values of $(1 + \sigma)$ so that the rates of advance of the individual fronts in the various passages will be the same in both tubes.

At any time the values of c, and therefore those of dc/dX and dc/dx, will be the same in both tubes. This shows that Δ can only be a function of the geometry of the packing and of $u/(1 + \sigma)$.

Since *ex hypothesi* it is independent of u it must also be independent of σ.

For concentrations so small that variations of u are negligible ordinary diffusion theory can be used. This gives

$$\frac{dc}{dx} = \pm \frac{c_1}{(4\pi \Delta X)^{1/2}} \exp\{-(x - X)^2/4 \Delta X\}$$

The sign is negative for saturation and positive for elution conditions.

Let δ_0 be the difference of the values of x at the 90 per cent and 10 per cent points when the concentrations are small. From tables of the Error Function, $\delta_0 = 3{\cdot}625(\Delta X)^{1/2}$ so that $S_0 = 3{\cdot}625(\Delta/L)^{1/2}$ where L is the tube length and $d\delta_0/dX = LS_0^2/2\delta_0$.

In certain circumstances the front can advance without change of form, when $dc/dX = -dc/dx$ and the equation reduces to

$$\Delta \frac{dc}{dx} = -\frac{\sigma c}{1 + \sigma} \cdot \frac{c_1 - c}{1 - \frac{\sigma}{1 + \sigma}(c_1 - c)}$$

$$\therefore \qquad \frac{dx}{d \log \left(\frac{c_1 - c}{c} \right)} = \frac{\Delta}{c_1} \cdot \frac{1 + \sigma}{\sigma} \left\{ 1 - \frac{\sigma}{1 + \sigma}(c_1 - c) \right\}$$

If c varies between values equidistant above and below $\frac{1}{2}c_1$ the mean value of c will be $\frac{1}{2}c_1$ so that

$$\delta = \frac{\Delta}{c_1} \cdot \frac{1 + \sigma}{\sigma} \left(2 - \frac{\sigma}{1 + \sigma} c_1 \right) \log 9$$

Since c must always lie between c_1 and zero the value of dc/dx can only be negative and the equation can only hold for saturation. Calling this quantity δ_s the asymptotic upper limit of S for saturation is $\delta_s/L = S_s$. Combining the two equations we have for saturation conditions

$$\frac{d\delta}{dX} = \frac{LS_0^2}{2} \left(\frac{1}{\delta} - \frac{1}{\delta_s} \right)$$

This gives

$$\log \frac{1}{1 - S/S_s} - \frac{S}{S_s} = \frac{1}{2} \left(\frac{S_0}{S} \right)^2$$

Now $\Delta/L = S_0^2/13{\cdot}14$ so that

$$\frac{S_0}{S_s} = \frac{2{\cdot}99 c_1}{S_0} \Big/ \left(\frac{1 + \sigma}{\sigma} \quad \frac{1}{2} c_1 \right)$$

The equation is easily solved by trial.

Table IV. Saturation

S/S_0	1·0	0·9	0·8	0·7	0·6	0·5	0·4	0·3
S_s/S_0	∞	3·24	1·57	1·01	0·72	0·538	0·4075	0·3004

If c_1 is small

$$S = S_0 - \frac{2{\cdot}99}{3} \cdot \frac{\sigma}{1+\sigma} c_1$$

If δ is large the value of dc/dx will be small compared to that of c so that the equation becomes

$$\frac{dc}{dX} = -\frac{1 - \dfrac{\sigma}{1+\sigma} c_1}{\left(1 - \dfrac{\sigma}{1+\sigma} c\right)^2} \cdot \frac{dc}{dx}$$

Let $c = f(\varphi)$ where $\varphi = (x - X)/X$

Then

$$\frac{dc}{dX} = -\frac{x}{X^2} \cdot \frac{dc}{d\varphi}$$

$$\frac{dc}{dx} = \frac{1}{X} \cdot \frac{dc}{d\varphi}$$

$$\therefore \qquad \frac{x}{X} = \frac{1 - \dfrac{\sigma}{1+\sigma} c_1}{\left(1 - \dfrac{\sigma}{1+\sigma} c\right)^2}$$

if $dc/d\varphi$ is not zero.

Clearly dc/dx can only be positive so that the equation can only apply to elution conditions. At the tube exit $x = L$ and X is proportional to the time elapsed since the change of inlet composition, so that

$$S_e = \left\{\left(1 - 0{\cdot}1 \frac{\sigma}{1+\sigma} c_1\right)^2 - \left(1 - 0{\cdot}9 \frac{\sigma}{1+\sigma} c_1\right)^2\right\} \Big/ \left(1 - 0{\cdot}5 \frac{\sigma}{1+\sigma} c_1\right)^2$$

$$= 1{\cdot}6c_1/[(1+\sigma)/\sigma - \tfrac{1}{2}c_1]$$

This is independent of X so that δ_e grows at a constant rate if diffusion is negligible. Combining this equation with the diffusion equation as before

$$\frac{d\delta}{dX} = \frac{LS_0^2}{2\delta} + S_e$$

This gives

$$\frac{S}{S_0} - \frac{S_e}{S_0} = \frac{S_0}{2S_e} \log\left(1 + 2\frac{S}{S_0} \cdot \frac{S_e}{S_0}\right)$$

Developing as a series for small values of S_e

$$\left(\frac{S}{S_0}\right)^2 = 1 + \frac{4}{3}\frac{S^3 S_e}{S_0^4} = 1 + \frac{4}{3} \cdot \frac{S_e}{S_0} \text{ approximately}$$

This gives

$$S = S_0 + \tfrac{2}{3}S_e$$

$$= S_0 - \frac{3{\cdot}2}{3} \cdot \frac{\sigma}{1+\sigma} c_1$$

This closely resembles the corresponding formula for saturation. The sign of the c_1 term is reversed as would be expected and its coefficient is a few per cent greater.

Table V. Elution

S/S_0	S_e/S_0	*Difference*	S/S_0	S_e/S_0	*Difference*
1·0	0·000	1·000	4	3·521	0·479
1·25	0·356	0·894	5	4·580	0·420
1·5	0·685	0·815	6	5·624	0·376
1·75	0·997	0·753	7	6·660	0·340
2	1·298	0·702	8	7·687	0·313
2·5	1·877	0·623	∞		$\frac{S_0}{S_e} \log \frac{S_e}{S_0} \sqrt{2}$
3	2·436	0·564			
3·5	2·983	0·507			

The difference of the coefficients is not real; it is due to neglect of the fact that during elution the concentration gradient becomes more linear as time goes on and vice versa. The difference is not large enough to be important.

Table V gives solutions of the equation for various values of S_e/S_0. *Table VI* gives the results of comparison with experiment. Most of the work

Table VI. Comparison with Observation

Saturation	S/S_0	0·9	0·8	0·7	0·6	0·5	0·4	0·3
$S_0 = 0{\cdot}10$	c_1% *Calc.*		3·0	4·7	6·5	8·6	10·8	15·1
	c_1% *Obs.*		2·8	4·7	7·0	12	20	>30
$S_0 = 0{\cdot}17$	c_1% *Calc.*	2·5	5·0	7·8	10·9	14·5		
	c_1% *Obs.*	2·6	5·0	7·7	12	18		
Elution	S/S_0	1·25	1·5	1·75	2	3·5	6	
$S_0 = 0{\cdot}10$	c_1% *Calc.*	3·1	6·0	8·7	11·1	24·3	42·6	
	c_1% *Obs.*	3·2	6·0	8·1	10·2	19	28	
$S_0 = 0{\cdot}17$	c_1% *Calc.*	5·4	10·1	14·4	18·4			
	c_1% *Obs.*	6·3	10·2	13·3	16			

was carried out with nitrogen as carrier and propane as vapour for which $S_0 = 0{\cdot}10$ in the tube used. A few runs with the same tube were made with hydrogen and propane, when $S_0 = 0{\cdot}17$.

A value of $\sigma/(1 + \sigma) = 0{\cdot}70$ was used for the purpose of computing calculated values.

The best fit for values of c_1 up to 10 per cent was given by assuming that $\sigma/(1 + \sigma) = 0{\cdot}70$ and mixture concentrations were calculated corresponding to various round number values of S/S_0. Observed values were read off from a smoothed curve.

For values of S/S_0 between 0·6 and 1·8 the agreement of theory and observation is probably within experimental error; beyond these points the agreement rapidly deteriorates, the observed values of S being greater than the calculated values for both saturation and elution.

The theory is adequately confirmed for a range of concentrations which should cover most practical cases.

If the tube is initially full of pure carrier and a short 'slug' of mixture of high vapour concentration is suddenly introduced followed by pure carrier then let $c = (\Delta/X)^{1/2} f(\psi)$ where $\psi = (x - X)/(\Delta X)^{1/2}$. X here is $u_0 t/(1 + \sigma)$, the distance travelled in time t by a front of low concentration.

With this definition of X

$$\frac{dc}{dX} = -\frac{\dfrac{dc}{dx} - \Delta \dfrac{d^2c}{dx^2}}{\left\{1 - \dfrac{\sigma}{1+\sigma}\left(c - \Delta \dfrac{dc}{dx}\right)\right\}^2}$$

If $\Delta\, dc/dx$ is small compared to c and c^2 is small compared to unity the equation can be simplified to

$$-\frac{dc}{dX} = \frac{dc}{dx} + \frac{2\sigma}{1+\sigma} c \frac{dc}{dx} - \Delta \frac{d^2c}{dx^2}$$

Now

$$-\frac{dc}{dX} = \frac{\Delta^{1/2}}{2X^{3/2}}\left\{f(\psi) + \frac{x+X}{(\Delta X)^{1/2}} f'(\psi)\right\}$$

$$\frac{dc}{dx} = \frac{1}{X} f'(\psi) \qquad \frac{d^2c}{dx^2} = \frac{1}{\Delta^{1/2} X^{3/2}} f''(\psi)$$

Substituting these values in the equation gives

$$\frac{1}{2}\left\{f(\psi) + \psi f'(\psi)\right\} = \frac{2\sigma}{1+\sigma} f(\psi) f'(\psi) - f''(\psi)$$

Integration with respect to ψ gives

$$\frac{1}{2}\psi f(\psi) = \frac{\sigma}{1+\sigma} f^2(\psi) - f'(\psi)$$

Let $Y = (1 + \sigma)/\sigma\, f(\psi)$, then

$$\frac{1}{2}\psi Y = 1 + \frac{dY}{d\psi}$$

The solution of this equation is

$$Y = Ae^{\psi^2/4} - \pi^{1/2}\left\{\frac{(\psi^2/4)^{1/2}}{\frac{1}{2}!} + \frac{(\psi^2/4)^{3/2}}{\frac{3}{2}!} + \cdots\right\}$$

If ψ is large the second term approaches $-\pi^{1/2}e^{\psi^2/4}$ so that since Y must always be positive and must go to infinity for large positive or negative values of ψ (where c is zero) the value of A must exceed $\pi^{1/2}$. Any value of A satisfies the equation.

The total quantity of vapour in the slug can be found from the value of $(1 - \sigma)\int c\,dx$, the length of tube which it would fill in the pure state if the packing were inert. This is equal to

$$A(1+\sigma)\int f(\psi)\,d\psi = A\frac{(1+\sigma)^2}{\sigma}\int\frac{d\psi}{Y} = \frac{S_0^2 L}{13{\cdot}14}\cdot\frac{(1+\sigma)^2}{\sigma}\int\frac{d\psi}{Y}$$

The value of $\int_{-\infty}^{+\infty}\frac{d\psi}{Y}$ depends on the value of A. The value of the integral has been worked out for several values of A: in addition the position of the minimum [the maximum of $f(\psi)$], the corresponding value of $f(\psi)$ and the positions of the points where $f(\psi)$ falls to 10 per cent of the maximum were determined.

$$\psi = \frac{3{\cdot}625}{S_0}\cdot\frac{x - X}{(LX)^{1/2}} = \frac{3{\cdot}625}{S_0}\cdot\frac{x - L}{L} \quad \text{at the exit}$$

If t' is the time taken by a very small slug of vapour to travel along the tube then

$$\psi' = \frac{3{\cdot}625}{S_0}\cdot\frac{t' - t}{t} = \frac{3{\cdot}625}{S_0}\cdot\frac{t' - t}{t'} \quad \text{approximately}$$

Table VII gives values of $\psi/3{\cdot}625$ for the maximum and the two 10 per cent points for various values of $(1/13{\cdot}14)\int(1/Y)\,d\psi$. The column headed $Width/S_0$ gives the difference of the values of t/t' for the two 10 per cent points.

Table VII

$\frac{\sigma}{(1+\sigma)^2 S_0^2}\cdot\frac{1+\sigma}{L}\int c\,dx$	$\frac{t'-t}{S_0 t'}$ 10%	*Maximum*	10%	$Width/S_0$
0·00	0·837	0·000	−0·837	1·674
0·136	1·005	0·276	−0·695	1·700
0·28	1·195	0·55	−0·575	1·77
0·63	1·62	1·10	−0·39	2·01
1·10	2·09	1·65	−0·26	2·35
1·68	2·58	2·20	−0·15	2·73

Mutual effect of two vapours

The phenomena illustrated by *Table VII* have an effect on the separation of two vapours with slightly different σ.

Consider the case of a vapour containing a small quantity of an impurity having the adsorption ratio σ'. Consider first the case where σ' is greater than σ. The impurity will lag behind the main body of vapour. While they are still mixed any variations of u affect both equally so that the concentration effect has no influence on the rate at which they separate but the region in which the two vapours overlap is in the tail of the main body. If the quantity of vapour is large the value of A is very close to $\pi^{1/2}$ and the distribution in the tail is independent of the quantity present. For values of ψ less than -1 the value of c is very nearly given by

$$c = \frac{1+\sigma}{2\pi^{1/2}\sigma}\left(\frac{A}{X}\right)^{1/2} e^{-(X-x)^2/4AX}$$

$$A = S_0^2 L/13{\cdot}14$$

and at the exit $X = L$ so that

$$c = 0{\cdot}078\,\frac{1+\sigma}{\sigma}\,S_0 e^{-\frac{3{\cdot}285}{S_0^2}\left(\frac{t-t'}{t'}\right)^2}$$

Ordinary diffusion theory, neglecting concentration effect on velocity, gives

$$c = \frac{1{\cdot}81}{\pi^{1/2}}\,\frac{\int c\,dx}{S_0 L}\,e^{-\frac{3{\cdot}285}{S_0^2}\left(\frac{t-t'}{t'}\right)^2}$$

Equating these gives

$$\frac{\sigma}{1+\sigma}\,\frac{\int c\,dx}{S_0^2 L} = 0{\cdot}076$$

For larger values of $\int c\,dx$ the concentration effect reduces the value of c in the tail of the main body and so increases the ease of resolution of the peaks. A large slug of gas increases the size of the impurity peak but has no influence on the main peak in the region of overlap.

The equations for the case where $\sigma' < \sigma$ are very difficult but an approximation to the concentration effect can be obtained by neglecting diffusion.

If A is zero and c not too large then

$$c = \frac{1+\sigma}{2\sigma}\cdot\frac{x-X}{X}$$

$$\int c\,dx = \frac{1+\sigma}{4\sigma}\,\frac{(x-X)^2}{X}$$

At this value of $(x - X)$ the value of c abruptly falls to zero. c is a maximum at the front where

$$c^2 = \frac{1+\sigma}{\sigma X}\int c\,dx$$

At any point within the range of non-zero c,

$$\frac{u}{u_0} = 1 + \frac{\sigma}{1+\sigma}\,c$$

neglecting terms in c^2.

The rate of travel of the impurity is $u/(1+\sigma')$.
If the distance it has travelled is X' then

$$\frac{dX'}{dX} = \left(\frac{1+\sigma}{1+\sigma'}\right)\left(1+\frac{\sigma}{1+\sigma}c\right)$$

$$= \left(\frac{1+\sigma}{1+\sigma'}\right)\left(1+\frac{1}{2}\cdot\frac{X'-X}{X}\right)$$

$(x-X)/X$ must of course lie within the limits of non-zero c. If $\sigma - \sigma' \quad (\delta\sigma)$ and this is small

$$\frac{dX'}{dX} = 1+\frac{(\delta\sigma)}{1+\sigma}+\frac{1}{2}\cdot\frac{X'-X}{X}$$

$$\therefore \qquad \frac{X'}{X} = \frac{dX'}{dX} = 1+2\ \frac{(\delta\sigma)}{1+\sigma}$$

$$\frac{X'-X}{X} = 2\ \frac{\delta\sigma}{1+\sigma}$$

$$c = (\delta\sigma)/\sigma$$

This holds so long as

$$\frac{(\delta\sigma)^2}{\sigma^2} \leqslant \frac{1+\sigma}{\sigma X}\int c\,dx$$

i.e. when

$$\frac{X}{L} < \frac{\sigma(1+\sigma)}{(\delta\sigma)^2}\cdot\frac{\int c\,dx}{L}$$

If the quantity is less than unity then at the tube exit

$$\frac{X'}{X} = 1+\frac{(\delta\sigma)}{(1+\sigma)}\left\{1+\frac{\sigma(1+\sigma)}{(\delta\sigma)^2}\cdot\frac{\int c\,dx}{L}\right\}$$

As an example if

$$\frac{(\delta\sigma)}{(1+\sigma)S_0} = 2$$

then

$$\frac{X'-X}{X} = 2S_0\left\{1+\frac{1}{4}\frac{\sigma}{(1+\sigma)}\cdot\frac{\int c\,dx}{S_0^2 L}\right\}$$

From Table VII

$\frac{\sigma}{1+\sigma}\cdot\frac{\int c\,dx}{S_0^2 L}$	$\frac{X'-X}{S_0 X}$ *impurity*	$\frac{X'-X}{S_0 X}$ 10% *point*	*Difference*
0·00	2·00	0·837	1·163
0·136	2·068	1·005	1·063
0·28	2·14	1·195	0·945
0·63	2·315	1·62	0·695
1·10	2·55	2·09	0·46
1·68	2·84	2·58	0·26

The 10 per cent points of the two peaks coincide when the difference is 0·837 so that the peaks would not be separated if

$$\frac{\sigma}{(1+\sigma)} \cdot \frac{\int c\,\mathrm{d}x}{S_0^2 L}$$

exceeded about 0·3. This makes a small quantity of an impurity difficult to detect if its value of σ is only slightly less than that of the main body.

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DISCUSSION

A. Klinkenberg: The foregoing paper draws attention to an observed asymmetry between saturation and elution, this being so with a linear isotherm, while other authors generally attribute asymmetry to non-linear isotherms. Among the latter, my colleagues, Dr Keulemans and Mr Kwantes, were mentioned. We have therefore been induced to trace the possible causes of this discrepancy.

In the normal course of gas liquid partition chromatography, isotherms being linear, when a peak is introduced, a gaussian probability curve is obtained with a width proportional to the square root of the length of the column, and correspondingly, with a height inversely proportional to that root. I may, in this respect, refer to the two forthcoming papers mentioned by Dr Keulemans.

On the basis of such theories, in the event of displacement one expects an integrated gaussian curve. Its width will be proportional to the root of the length and it will be identical for saturation and elution.

Bosanquet and Morgan's curves are indeed probability integral curves. *Figure 2* is, of course, too schematical to see it, but the text says on page 38, that a straight line is obtained on probability paper, which is, of course, adequate proof. However, the width increases in proportion to the *first* power of the column length and the curves differ for saturation and elution, only becoming identical upon extrapolation to zero concentration.

This difference between theory and experiment calling for an explanation, the authors then present a theory in which the change is linear, velocity upon adsorption or desorption being called in to produce the asymmetry.

We should like to observe that the method of introducing the variation of the linear velocity in the calculations does not appear to us to be correct. It is assumed that in passing the transition region during saturation, a fraction $\sigma/(1 - \sigma)$ of the solute is removed, presumably because this is the fraction of the total solute always at a standstill. This, however, applies at each contact stage and so the effect of the transition region must be to remove the solute completely.

I therefore fail to see the usefulness of the fraction $\sigma/(1 - \sigma)$ at the beginning of the calculation and at many later places. The equation

$$\frac{\mathrm{d}c}{\mathrm{d}X} = -\frac{\mathrm{d}c}{\mathrm{d}x} + A\,\frac{\mathrm{d}^2 c}{\mathrm{d}x^2}$$

at the bottom of page 42 is again correct. It is well known, if t replaces X. I think I may quote a 1955 paper* by Glueckauf in this respect. However, the condition of low concentrations, used in its derivation, also implies constant forward velocity. A quicker derivation then is possible from the material balance equation

$$(1 + \sigma)\frac{dc}{dt} = \frac{d}{dx}\left\{u\left(c + 1\frac{dc}{dx}\right)\right\} = 0$$

with $X = u_1 t/(1 + \sigma)$ by equating $u = u_1$ (= constant).

In this line of thought the basic idea of varying velocities at this point is therefore lost.

In the middle of page 43 interest is shown in the study of fronts of constant shape, where

$$\frac{dc}{dX} = -\frac{dc}{dx}$$

To me this indicates that $1 = 0$ and I have not been able to follow the deductions regarding the value of dc/dx. Moreover, I have failed to see what interest there could be in fronts of constant shape, considering that the experiments do not produce them.

One thing that could help to make the paper more convincing would be to number the equations and indicate more clearly the sequence of arithmetical operations.

Pending such matters I would hazard a guess regarding quite a different explanation, namely, that thermal effects play a role. In displacement these might be much stronger than in elution of peaks, where the concentration diminishes rapidly from the peak.

Considering that heat is evolved upon saturation and absorbed upon elution, the effect would be of the right sign. Moreover, it would be independent of column temperature, of carrier gas rate and of viscosity, as observed.

A quantitative theory, involving coupled chromatographic equations for mass and heat flow would be very difficult, but perhaps temperature measurements could be made.

To cut a long story short, having started to discuss linear isotherms, I do not doubt the linearity but I question instead the isothermal behaviour.

C. H. Bosanquet: In reply to Dr Klinkenberg the equation at the bottom of page 42 does not imply that all the terms dependent on concentration have been abandoned. The fact that the full equation reduces asymmetrically to the simple form when c is small was used simply as a check on the analysis.

The mathematics on page 43 are rendered somewhat obscure by a misprint in the eighteenth line†. Integrating both sides with respect to x, the rest of the analysis follows easily.

Dr Klinkenberg suggests that some thermal effect may be responsible for the observed asymmetry but he has not produced the necessary equations, far less asked for them. The theory developed in our paper gives quite close quantitative agreement with experiments without introducing any adjustable constants at all. My confidence in the theory is based on this quantitative agreement which I consider the ultimate test.

Incidentally the group of peaks shown in *Figure 3* of Pollard and Hardy's paper (p 122) shows excellent agreement with the predictions of the theory.

* *Trans. Faraday Soc.* **51**, 34, 1955.

† This has since been corrected—Ed.

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5

A BASIS FOR THE COMPARISON AND CHOICE OF SOLVENTS IN VAPOUR PHASE PARTITION CHROMATOGRAPHY

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The general applicability of the logarithmic relation between the retention volume and the saturation vapour pressure of a solute at the elution temperature is further demonstrated and three new examples of the 'family' plot are given. The usefulness of the $\log v'/\log p$ and inverse temperature dependence plots in the quantitative comparison and choice of solvent and of experimental conditions is discussed and examples of their use for this purpose are given. A concise method of compilation of elution data is suggested.

THE rapid emergence of vapour phase chromatography into the front rank of analytical techniques emphasizes, if emphasis is needed, the remarkable power of the method. In a surprisingly short time many separations of a wide variety of substances have been reported and advances in instrumentation have been equally rapid. The literature, however, contains relatively little information relating to the effect of temperature variation on the retention volume and what data there are relate only to few solvents. It is highly probable that much data of this sort remain unpublished and it is undoubtedly desirable that this should be remedied.

It is obvious that the retention volume of any solute should be connected with its saturation vapour pressure at the temperature of elution and this was, in fact, pointed out early by James and Martin[1]. This aspect received scant attention until recently, however, when it was shown[3,4] that the relation could be expressed logarithmically. Thus

$$\log v' = -a \log p + \text{constant}$$

where $v' = v_0(1 + \beta t)$, v_0 = the measured retention volume reduced to s.t.p., β = the temperature coefficient of expansion of the solvent, $a = \Delta H^s / \Delta H^v$, the ratio of the molar heat of solution at infinite dilution to the molar latent heat of vaporization, and t = the elution temperature in °C.

The constant term contains quantities relating to column parameters, the molar volume of the solvent at 0 C, the gas constant R, and the solubility coefficient α of the solute in the particular solvent. If v' is corrected for the pressure drop across the column (James and Martin[1,2]), as is strictly necessary for comparison purposes, then v' may be replaced by v'_p. Provided the pressure drop is maintained constant v' is, however, adequate for this purpose.

Substitution for $\log p$ by the conventional vapour pressure equation leads

to an inverse temperature dependence of the logarithm of the retention volume such as has been demonstrated by Littlewood, Phillips and Price[5], Hoare and Purnell[3,4], and mentioned by Bradford, Harvey and Chalkley[6]. These relations are clearly limited in their application by the assumptions made in their derivation but the experimental evidence indicates that they hold over a surprisingly wide range of temperature. *Figures 1–5*, for instance, show that the linear plot of the data frequently extends up to vapour pressures of several atmospheres.

It is the purpose of this work to indicate, in some measure, the manner in which much useful information may be gained regarding solvent efficiencies (as distinct from column efficiency) and the choice of column lengths and operating conditions by consideration of the elution data in the light of the above relations.

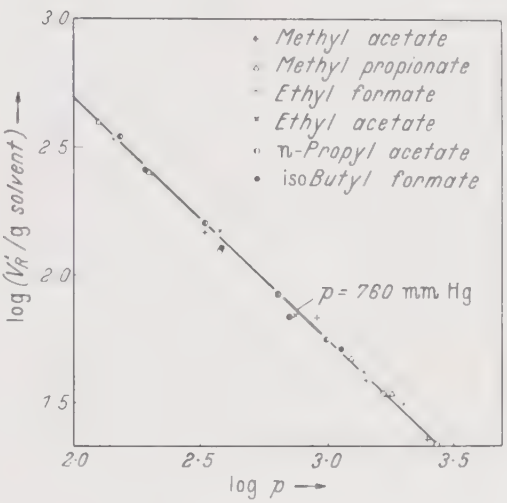

Figure 1. Family retention diagram for some esters on silicone oil (702)

The family plot

The usefulness of the log $v'/(1/T)$ plots is immediately obvious but they frequently may not yield all of the available information relating to a particular solute/solvent system. One of the most interesting findings reported previously[3,4] was that the log v'/log p plots (designated the retention diagrams) for homologues and certain other related compounds were often superimposed. This was demonstrated for a variety of aliphatic hydrocarbons, aliphatic alcohols, ketones and some chlorohydrocarbons on columns containing two phthalate esters and liquid paraffin. The lack of extensive temperature variation data in the literature limits the investigation of the extent of this phenomenon but further examples, drawn from the results of Littlewood, Phillips and Price[5], are given in *Figures 1–3*. These illustrate the retention diagrams for a number of esters, and alcohols on columns of silicone oil and tritolyl phosphate respectively, and it may be considered somewhat surprising first, that such a diversity of esters gives a family plot for both solvents, and secondly, that tritolyl phosphate is apparently so unselective compared to the silicone oil particularly with the alcohols. When family plots are obtained it is evident that solubility differences play little or no part and that the separation process is purely one of extractive distillation.

The slopes of the lines (i.e. a) are, in each case, fairly close to unity, thereby indicating relatively ideal behaviour. It has been pointed out that for a family a value of a in excess of unity gives rise to a 'superdistillation' while a

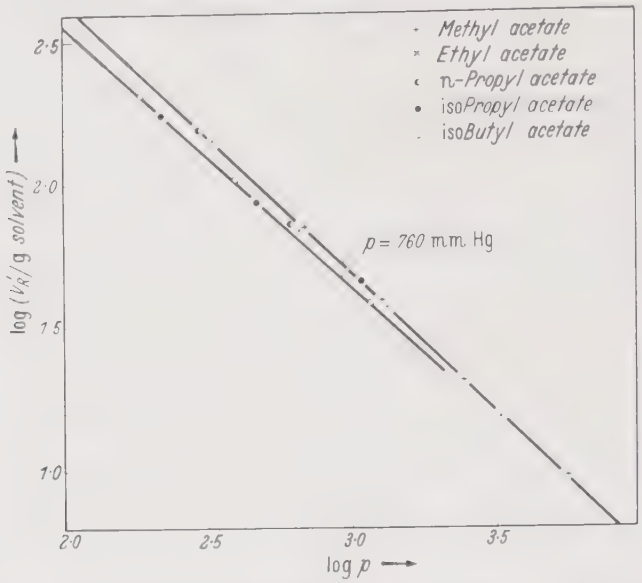

Figure 2. Family retention diagram for some esters on tritolyl phosphate

value less than unity represents an effective decrease in the solvent efficiency. Obviously, where family retention diagrams are obtained for a series of solutes on several solvents the best solvent is that for which a is largest since

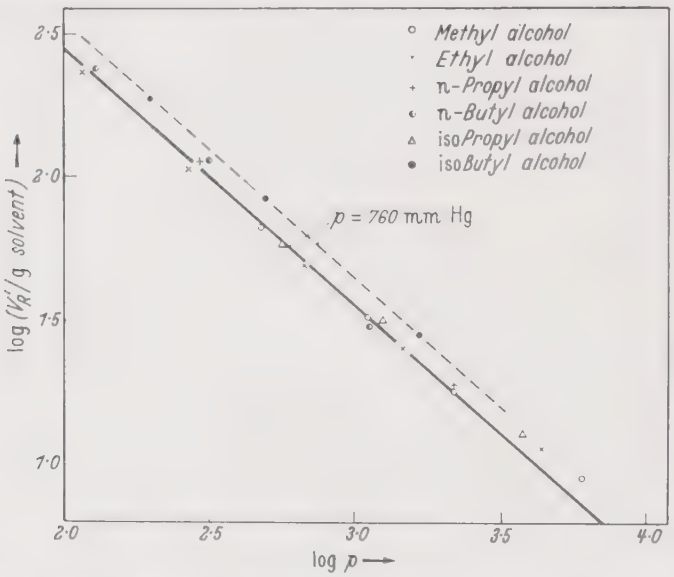

Figure 3. Family retention diagram for aliphatic alcohols on tritolyl phosphate

this represents the highest retention volume ratio per unit difference of vapour pressure between any two solutes.

Since the available evidence covers a fairly wide range of solutes in four or five solvents it may be taken with some confidence that such family diagrams are to be expected fairly frequently.

Alternative types of retention diagram

The various types of retention diagrams to be expected theoretically for a pair of solutes in the same solvent have been discussed at length elsewhere[1] and they need only be summarized here. Depending on the relative values of a and α, the following cases may arise:

(*a*) Increasing temperature may lead either to increasing or decreasing resolution.

(*b*) Decreasing resolution may lead to crossing of the retention diagrams in consequence of which there may be an upper and a lower elution temperature at which the separation, in terms of the relative retention volumes, will be the same with a reversal in the order of elution.

It is most likely that the latter cases will be very uncommon and that increasing temperature will normally lead to decreasing resolution.

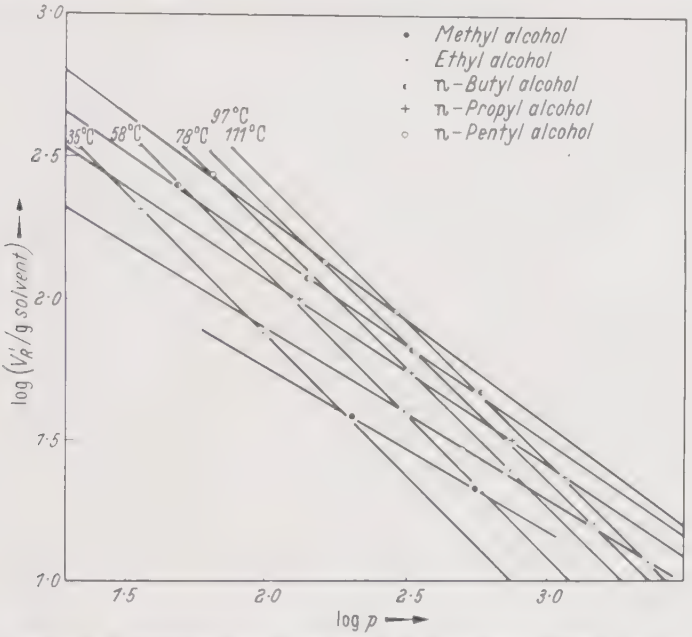

Figure 4. Retention diagrams for n*-aliphatic alcohols on silicone oil (702) illustrating the 'grid' effect with solubility differences enhancing separation due to vapour pressure differences*

The grid effect

As several authors have pointed out, the solvent for any analysis may be chosen such that solution effects are superimposed on the differential vapour pressure between solutes. In consequence, for a mixture of chemically unrelated solutes the retention diagrams will probably be widely spaced and, of course, this may also be the case for solutes of similar type. It does not necessarily follow, however, that the two effects work together so as to enhance separation.

As an example of this the data[5] for some normal alcohols on a silicone oil column and for some aromatic hydrocarbons on tritolyl phosphate are plotted in *Figures 4* and *5* respectively. The retention diagrams for the individual members of each series are linear over the temperature range studied, the alcohols showing slightly increasing values of a with increasing molecular

weight (0·60–0·65). Linear isotherms, however, can be drawn for each series and the resultant diagram resembles a grid. The slopes of the isothermals are all very close to unity and we may consider that while each alcohol exhibits positive deviation from Raoult's law the increasing solubility with molecular weight tends to 'straighten up' the isothermals such that an ideal slope is attained. Thus, in this system, vapour pressure and solubility differences are complementary.

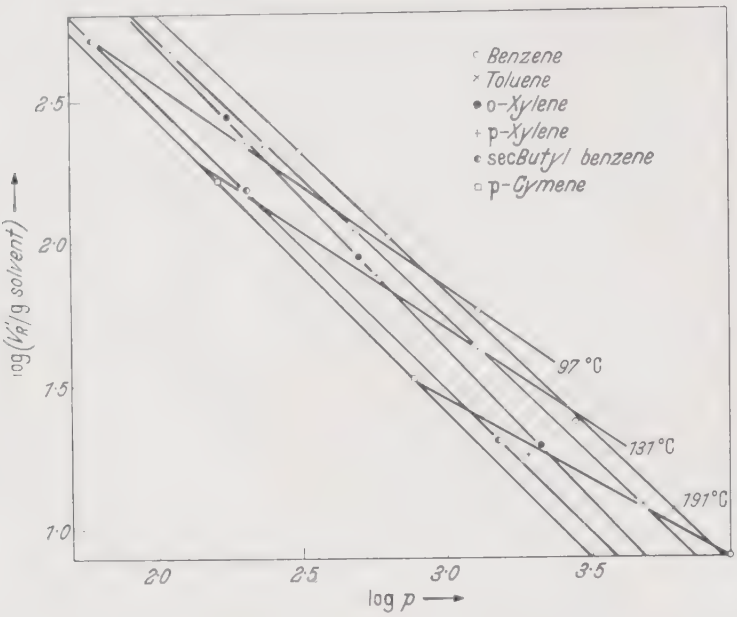

Figure 5. Retention diagrams for some aromatic hydrocarbons on tritolyl phosphate showing 'grid' effect with solubility differences diminishing separation due to differential vapour pressures

A similar grid-type diagram is obtained for some aromatic hydrocarbons (*Figure 5*) although, since they are, perhaps, not so closely related, the fit along the isothermals is not so good as for the alcohols. In this system, the vapour pressure and solubility differences act in opposition and the individual member plots have values of a close to unity while the isothermals have values of about 0·7. The resolution, in consequence, is decreased by this factor since the components of higher vapour pressure also have the higher solubilities. It may be considered that systems such as these give rise to pseudo family plots the slopes of which vary with the elution temperature.

The behaviour of the aromatics on silicone oil is generally similar to that obtaining on tritolyl phosphate but the separation of the individual plots is nothing like so marked as in the latter case. The diagram is not reproduced since the lines fall so closely together that illustration is difficult. The slopes of the individual retention diagrams are close to unity while the isothermals have a values of about 0·85. There is little doubt, therefore, that the silicone is the better all-round solvent for the aromatic hydrocarbons studied.

A system in which solution and vapour pressure effects both assist and oppose each other is illustrated in *Figure 6*, in which are shown the retention diagrams for some C_5 hydrocarbons on dioctyl phthalate columns. The ease

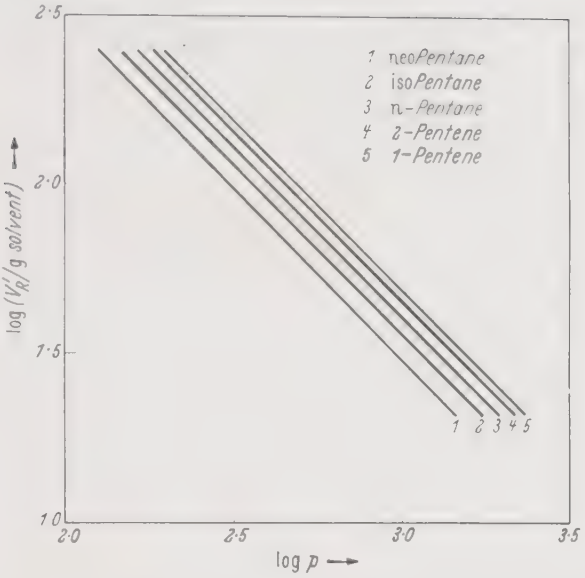

Figure 6. Retention diagrams for C_5 aliphatic hydrocarbons on dioctyl phthalate

with which paraffin isomers are separated is clearly due to the fact that solubility decreases with increasing vapour pressure of the components of the mixture. *Table I* lists the vapour pressures[9] at 20°C and values of V_b^0 for the hydrocarbons. It is immediately evident that the separation of *n*-pentane and 1-pentene will be the most difficult since here, in contrast, the component of

Table I

Substance	n-*Pentane*	iso*Pentane*	neo*Pentane*	1-*Pentene*	2-*Pentene*
$p_{20°}$	424	576	986	515	428
V_b^0	53·5	47·0	39·0	63·7	60·7

higher solubility also has the higher vapour pressure, the same being true to a lesser extent of the 1 and 2 olefins. *Table II* shows that a similar state of affairs exists when liquid paraffin is employed as the solvent except that the 2-olefin is here more soluble than the 1-olefin.

The analysis of such a mixture would thus, undoubtedly, be improved if a solvent of greater affinity for the olefins but of comparable efficiency for the isomeric paraffins could be found. Alternatively, of course, a solvent may be sought in which the affinity for olefins is less, thus in effect 'bringing on' the olefins relative to the *n*-paraffin. Bradford, Harvey and Chalkley[6] have demonstrated that this occurs when *iso*butene trimer is used as the solvent. On the whole, however, it would probably be better if a more efficient solvent could be found such that the olefins were retained longer. It may perhaps be said that, generally, the best solvent for any analysis will be one in which the solubilities of the solutes increase with decreasing vapour pressure.

The Compilation of Experimental Data

The rapid growth of the subject has resulted in an increasing amount of elution data becoming available. The major proportion of this is, however, in unsuitable form to be of quantitative use to other workers since it generally consists of illustrations of chromatograms with occasional tables of retention volumes, often in terms of relative retentions, and for unknown weights of solvent at a single temperature. Littlewood *et al.* have drawn attention to this point and in an attempt to make their results of general utility have given them in terms of the retention volumes per gramme of solvent. Even this expedient is insufficient to give a concise statement of the data over a range of temperature since the value at each temperature is necessary.

It is suggested that elution data may be most conveniently recorded by tabulation of the following quantities:

(*1*) molar heat of solution, ΔH^s

(*2*) retention volume per gramme of solvent at some standard temperature (e.g. 100 C), V_s^0

(*3*) slope a of the retention diagram

(*4*) retention volume per gramme of solvent at boiling point of solute, V_b^0.

The two retention volumes should be reduced to the values corresponding to zero pressure drop across the column by use of the appropriate equation[1,2].

It is evident that a knowledge of ΔH^s and V_s^0 immediately makes it possible to draw the inverse temperature plot since the former quantity enables calculation of the slope of the line while the latter gives an intercept at one temperature; similarly the values of a and V_b^0 enable the retention diagram to be drawn. All of the data for the particular solute/solvent system are thus given in terms of these four quantities, and workers interested in some particular analysis could determine from these values which solvents are likely to be the most suitable for their purposes without carrying out preliminary experiments. Thus, the values of a for various solvents would indicate the

Table II. Elution Data on Liquid Paraffin

Solute	a	ΔH^s	V_b^0	V_s^0
n-*Pentane*	0·99	5·99	44·8	8·2
n-*Hexane*	0·99	6·80	44·8	17·8
n-*Heptane*	0·99	7·32	44·8	40·0
1-*Hexene*	0·97	7·45	48·2	18·2
1-*Heptene*	0·97	8·78	48·2	39·5
1-*Octene*	0·97	10·00	48·2	82·1
2-*Pentene*	0·99	6·43	57·0	8·1
2-*Hexene*	0·99	7·60	57·0	26·0
2-*Heptene*	0·99	8·52	57·0	55·0
Ethyl alcohol	1·02	10·02	30·7	14·1
n-*Propyl alcohol*	1·02	11·00	30·7	31·2
n-*Butyl alcohol*	1·02	10·15	30·7	84·7
Methylene chloride	0·87	5·19	36·5	16·4
Chloroform	0·86	6·42	57·9	23·0
Carbon tetrachloride	0·86	6·62	57·9	33·0

direction and extent of deviations from ideal behaviour and, further, the existence of families would be immediately obvious since a and V_b^0 are identical for the various members. Finally, the inverse temperature plots indicate what would probably be the best temperature at which elutions should be conducted. As an illustration of this method of compilation, some data obtained for liquid paraffin columns are listed in *Table II*.

Applications to Experiment

The examples given here and elsewhere[1] illustrate most of the cases which in theory might arise. They underline the importance of the choice of elution temperature and also indicate clearly that a preliminary knowledge of the effect of temperature on the retention volumes of the components of a mixture is desirable before attempting any analysis for which no published data are available. It is possible that a temperature might well be chosen at which vapour pressure and solubility differences cancelled, in which event, much tedious experiment could lead only to no worthwhile result.

The support material

Little quantitative information is to be found relating to the possible influence of the support on the resolutions achieved in vapour phase chromatography. It is generally supposed that the material is completely wetted and inert and until conclusive evidence to the contrary is forthcoming it may reasonably be assumed that this is true.

Solvent, column length and elution temperature

Effective solvents are now known for a large number of analyses but it is evident that with the extension of the technique a rapid method of quantitative comparison of the effectiveness of various solvents in bringing about particular separations is desirable. Such a method would facilitate projected analyses not already recorded in the literature and might conceivably lead to improvement in some already reported. It is likely that the most useful method will incorporate the use of retention diagrams and the corresponding inverse temperature plots.

The advantage of this approach lies in the fact that the data may be obtained on relatively short columns provided only that the weight of solvent is known. The method is in itself rapid but the time taken for calibration becomes even less if members of a family are present in the mixture to be analysed. Elution of a single member provides all of the information for the series and the question of whether the series forms a family can be readily settled by elution of two fairly widely spaced members with subsequent elution of one of them at another temperature in order to determine whether or not a grid effect occurs.

From these calibration experiments the values of a, V_b^0, ΔH^s and V_s^0 can be obtained. The latter two quantities will enable a choice of elution temperature to be made, since in general this is just a matter of selecting the temperature at which there is maximum separation of the retention volumes for all the components of the mixture. Consideration of a and V_b^0 values will facilitate the choice of solvent and the latter value enables calculation of the probable length of column necessary to effect a complete resolution. The theoretical

plate theory of James and Martin[2] and the more recent treatment by Glueckauf[8] both yield an equation relating column efficiency, in terms of the number of theoretical plates, with the retention volume and band width. Since these quantities are determined for a particular column length in the calibration experiments it is possible to draw a predicted chromatogram for various lengths of column, the predicted retention volumes being modified in accord with any change in pressure drop with increased length of column. The choice of elution temperature should be made in conjunction with that of column length since a compromise between complete resolution and rapidity of elution may be necessary, particularly when minor components emerge late in the analysis.

As an example of the use of the method we may consider the retention diagrams for the esters on silicone oil and tritolyl phosphate (*Figures 1* and *2*). The slopes are virtually identical (0·94; 0·97), while the values of V_b^0 are 67·9 and 65·8 ml respectively. There is undoubtedly little to choose between the two solvents since the slightly lower value of a for silicone, if real, is offset by the slightly higher value of V_b^0. In the case of the *iso* esters some difference in the behaviour of the two solvents can be detected. The slopes are identical (0·90) but the V_b^0 values are 63·1 and 57·6 ml. The silicone is thus the better solvent for the separation of *iso* esters in virtue of the greater retention while tritolyl phosphate is superior for the separation of normal and *iso* esters in consequence of the greater differential solubility resulting in wider separation of the retention diagrams.

A comparison of some solvents in the separation of *n*-aliphatic alcohols (ethyl to pentyl) may be taken as another example. Tritolyl phosphate and liquid paraffin both yield family plots but V_b^0 is much greater for the former solvent and this would outweigh the slightly higher value of a in liquid paraffin. The ratio of retention volumes of successive alcohols in these solvents is sensibly constant (~2) over the temperature range 35–95°C. When silicone is employed, however, the grid effect results in an increase of V_b^0 with increasing temperature for each pseudo family diagram (16 ml at 58°C; 34·7 ml at 111°C). Although the values are always less than those on tritolyl phosphate comparison should not be based on this alone since, in consequence of the changing a values for the homologues, the relative retention volumes of adjacent members should increase with decreasing temperature. This is found to occur, the ratio at 78°C being the same as for the other two solvents while at 35°C the resolution is better by a factor of about 1·4. Thus at 80°C or above tritolyl phosphate appears to be more suitable while at temperatures lower than this the silicone is preferable.

Ray's data[7] for dinonyl phthalate as the solvent were illustrated elsewhere[1] as an example of a marked negative deviation from Raoult's law. The data were available only at 80 C and for an unknown weight of solvent so that it is impossible to calculate V_b^0 and also to determine whether the system exhibits a real or pseudo family diagram. Nevertheless, the a value of about 1·6 suggests that this solvent may well be the best of those under consideration for analysis of alcohols. This is borne out by calculation of the ratio of retention volumes of successive alcohols (~3) at 80 C. The versatility of this solvent remarked upon by Ray, therefore, seems to be a consequence of its ability to partake of specific interaction with polar solutes while behaving

ideally towards non-polar materials as evidenced by the near unit slope of the retention diagrams for hydrocarbons[4].

The author wishes to thank Professor R. G. W. Norrish for his continued encouragement and Mr M. R. Hoare for his frequent collaboration and much valuable discussion.

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DISCUSSION

C. J. Hardy: With respect to the superimposed $\log v'/\log p$ plots for chlorohydrocarbons we have found that on both DNP and silicone 702, CH_2Cl_2, $CHCl_3$, and CCl_4 do not give family plots, but exhibit complicated grid effects. On both liquid phases retention diagrams are obtained with slopes of *ca.* 1·09 for CH_2Cl_2 and $CHCl_3$, and *ca.* 0·95 for CCl_4.

On silicone 702 the isothermals joining $CHCl_3$ and CCl_4 have much lower slopes, *ca.* 0·5; the isothermals for CH_2Cl_2 and CCl_4, *ca.* 0·85; and for CH_2Cl_2 and $CHCl_3$, *ca.* 1·20. Hence for $CHCl_3/CCl_4$ and CH_2Cl_2/CCl_4 solubility differences diminish the separation due to vapour pressure differences, whereas the reverse is found for the pair $CH_2Cl_2/CHCl_3$.

On DNP the order of elution at any temperature is CH_2Cl_2 (first), CCl_4, $CHCl_3$. For the pair $CHCl_3/CCl_4$, the isothermals have a slope of *ca.* − 0·4 (i.e. negative with respect to the retention lines). In this case solubility differences completely reverse the separation due to vapour pressure differences. For $CH_2Cl_2/CHCl_3$ the slopes are +1·2 to +1·4 and here, as on silicone 702, the slopes are greater than unity and solubility differences tend to increase the separation due to vapour pressure differences.

Harrison in his paper also reports the deviation of these compounds from family plot behaviour on DNP and tricresyl phosphate.

A. T. James: In order to obtain the maximum use from published data I would suggest that the retention volumes of the substances studied relative to a standard substance be given. The corrected retention volume of the standard substance per gramme of stationary phase, column stationary phase and temperature would supply a complete set of data suitable for use by analysts and physical chemists. Different standards would be necessary for different temperatures and these should be related in the form of relative retention volumes.

E. Glueckauf: If one is looking for characteristic numbers by means of which the behaviour could be described with the minimum number of factors which are required, then surely one can use ordinary thermodynamic procedure of describing the system by giving the enthalpy, and the entropy with reference to one particular substance. This would then enable one to get the free energy differences, in other words, the equivalent value of γ in comparison to one standard substance, and would enable anyone to carry out the calculation just by means of knowing two values for any given temperature and any given system.

A. I. M. KEULEMANS: I fully agree with Dr Glueckauf's arguments, but I believe that what Dr James intended to say is that for most workers it will be more convenient to express data on gas chromatography in retention volumes rather than in terms of thermodynamic quantities. Also the contribution of workers with little experience in thermodynamics will then be made available.

E. GLUECKAUF: I would just like to add that in addition to these two values one might also supply the equation by means of which they can be used.

C. L. DUNN: Since equations for using retention volumes to obtain thermodynamic data have been mentioned I would like to put a simple equation on the board. The relationship

$$V_R^0 = V_m + HV_s$$

where V_m is the volume occupied by the mobile phase in the column, and V_s is that occupied by the gas phase, and H is the partition coefficient, has been presented by Dr Martin and co-workers here in the U.K. H can be expressed as $M_s RT/\gamma^0 p^0$ where M_s is the molal volume of the solvent.

p^0 is of course dependent only on the solute and T while γ^0 depends on both the solute and solvent. I propose that the committee on methods for reporting data consider the reporting of H values so that those interested in going farther can calculate the activity coefficients.

6

FACTORS AFFECTING KATHAROMETER SENSITIVITY AND COLUMN EFFICIENCY IN VAPOUR PHASE PARTITION CHROMATOGRAPHY

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A study has been made of the factors affecting the sensitivity of thermal conductivity cells (katharometers) used for detecting the zones emerging from a vapour phase partition chromatogram; greatest sensitivity is obtained when the ambient temperature is the lowest possible consistent with avoiding condensation.

A considerable increase in sensitivity has been obtained by burning the emergent zones over copper oxide and measuring (at laboratory temperature) the thermal conductivity of the carbon dioxide produced.

The effect has also been studied of changes in column temperature, column size, pressure, particle size of static phase support and 'load' size on the efficiency of a vapour phase chromatograph column; a fairly critical gas flow rate (depending on column diameter and particle size of the static phase support) has been found which gives best separations.

SINCE the separation of volatile mixtures by vapour-phase partition chromatography was first introduced by James and Martin[1], the technique has been extensively used and applied to a wide range of compounds.

Thermal conductivity cells (katharometers) have been the most widely used means of detecting and measuring the fractions emerging from the chromatograph column. The design of the katharometer itself has been largely an empirical matter, since for many problems adequate sensitivity has easily been obtained. In order to detect very small components, however, it was considered desirable to know the effect of the various factors which may influence the sensitivity.

Increased sensitivity was obtained by burning emergent zones from the chromatogram and measuring the resultant carbon dioxide in an infra-red gas analyser[2]. This procedure has the merit of producing relatively large volumes of carbon dioxide from most organic compounds and since carbon dioxide can be conveniently detected by a katharometer cell the sensitivity of this technique was compared with the normal vapour conductance measurements.

Since the detection of components is also limited by the degree of resolution (column efficiency) a more detailed knowledge of the factors affecting separation was required. The effect of the nature of the static phase has been

described by other workers and this investigation was therefore confined to the effect of other variables, e.g. column temperature, pressure, flow rate and column size.

Experimental

The apparatus consisted of a 3 ft long × 8 mm diameter straight column (except where described) packed with the appropriate filling and enclosed in a suitable electric furnace. The katharometer cell (see below) was attached to the end of the chromatograph column by means of a 'Quick Fit' joint and enclosed in a separate electric furnace. The exit pipe of the katharometer cell was connected via a simple trap and bubbler to a Hyvac pump; a stream of dry air was drawn in turn through a rotameter, a needle-type control valve, the chromatograph column, the katharometer cell, the trap and bubbler, and hence to the vacuum pump. Mercury pressure manometers were fitted to both inlet and outlet sides of the column. The samples were introduced on to the column through a rubber serum cap by means of a small hypodermic syringe.

The katharometer normally consisted of a 10 cm length of platinum wire (44 s.w.g.) in a 5 mm diameter glass envelope and was attached to the column via a Quick Fit joint; it was matched by an identical duplicate 'katharometer' completely sealed in a separate glass envelope and attached to it. The two katharometers formed two adjacent arms of a Wheatstone bridge network which was supplied by a 6 V battery. For convenience in measuring the peak heights a fairly wide range recorder was used, i.e. 30 mV F.S.D. Honeywell Brown.

Part I. Katharometer sensitivity

The effect on peak heights of changes in the katharometer ambient temperature and the platinum wire current was studied under standard conditions, i.e. Celite 545/silicone grease (60/40) column packing maintained at 250°C; outlet pressure 5 cm of mercury; flow rate 8 ml/min (760 mm of mercury); sample 'loads' of 0·04 ml of (*1*) C_{8-14} alcohols (approximately equal amounts), (*2*) ethylene glycol, (*3*) mixture of substituted malonic esters. The various types of katharometer which were studied were:

A. 10 cm of platinum wire (44 s.w.g.) made compact in the form of a spiral (about 4 cm long and of 1·5 mm coil diameter) passing centrally down a 5 mm diameter glass tube
B. 10 cm of platinum wire (44 s.w.g.) stretched taut in a 1·5 mm diameter glass tube
C. As (B) except glass tube of 5 mm diameter
D. As (B) except glass tube of 9 mm diameter
E. As (C) but with stainless steel tube in place of glass
F. As (A) except glass tube of 9 mm diameter
G. As (C) but with 48 s.w.g. platinum wire.

1. *Effect of katharometer ambient temperature*—The sensitivity (peak heights) was increased by lowering the temperature around the katharometer (for examples, see *Figure 1*). The most satisfactory temperature with respect to both sensitivity and base line drift (due to small temperature changes) is the lowest possible provided that condensation will not occur.

In addition to loss of sensitivity with high ambient temperatures, introduction of sample caused troughs to appear on the conductance record (which recovered slowly and would completely obliterate fast travelling components):

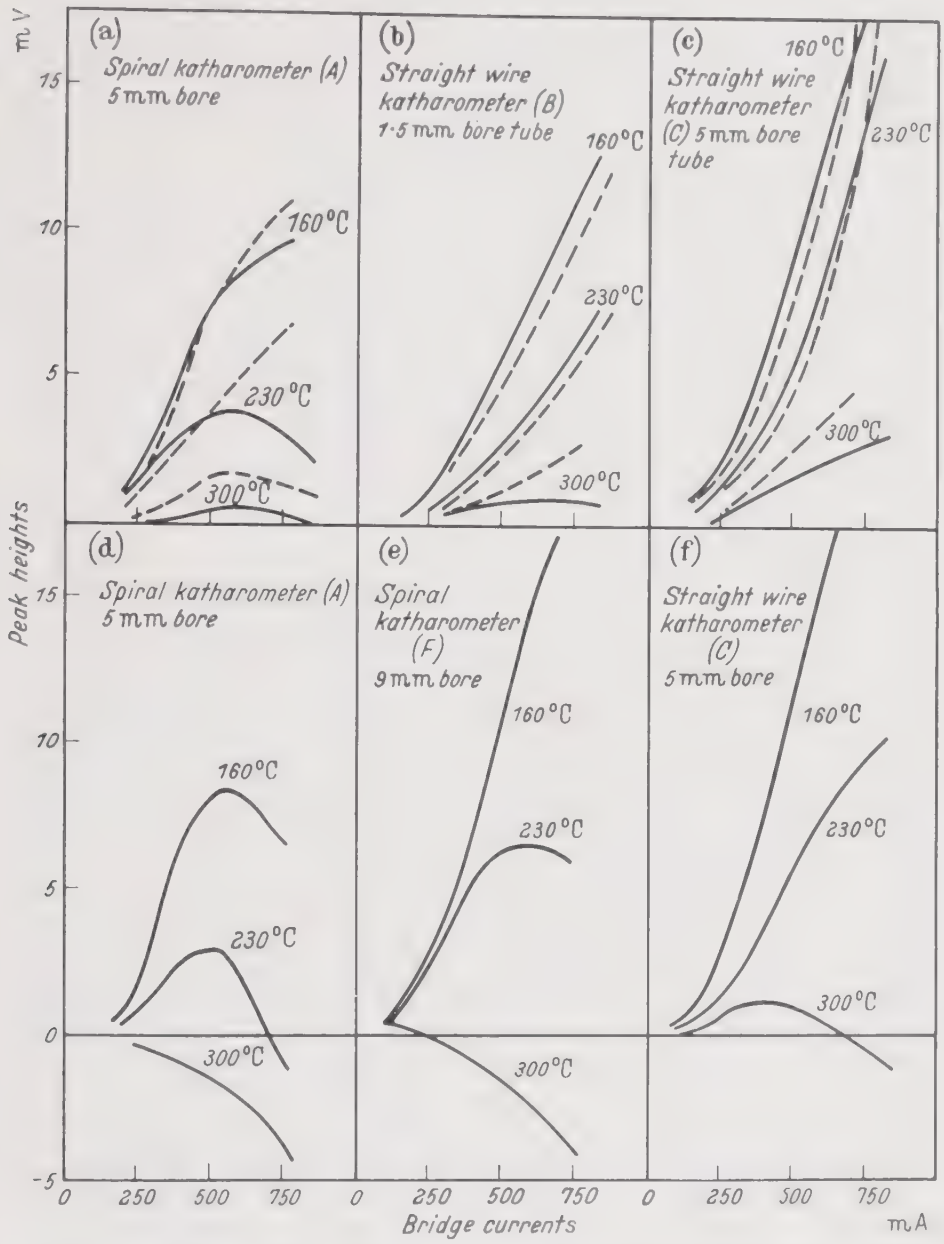

Figure 1. Effect of ambient temperature and bridge current changes on peak heights (a), (b), (c). *Octanol* ———; *decanol* – – –. (d), (e), (f). *Ethylene glycol*

very high ambient temperatures can also result in negative conductance peaks [*Figure 1*(d), (e)]. These effects must be borne in mind when deciding on katharometer temperature in the analysis of mixtures covering a wide boiling range.

2. *Effect of changes in katharometer current*—With the ambient temperature at a suitably low level the peak height sensitivity increased with increasing current through the platinum wire in the manner shown in *Figure 1*(c) (160 C). At rather higher ambient temperatures (230 C) this rate of increase was not so pronounced [*Figure 1*(f)] and at excessively high ambient temperatures (300 C) a decline in sensitivity was obtained with increasing current [*Figure 1*(f)]. This effect was more pronounced with the spiral platinum wire katharometers [*Figures 1*(a), (d) and (e)] and was attributed to the higher temperatures produced in the smaller compact cell. Any advantage this type of katharometer might possess by virtue of its smaller volume is therefore lost.

3. *Effect of cell diameter*—The sensitivity increased with increasing katharometer cell diameter [compare *Figures 1*(b) and (c)] but there is obviously a limit (depending on volume of the component zone) to the increase in sensitivity that can be obtained in this way; it was shown with trace components, i.e. 0·1 per cent octanol in decanol, that the peak height was decreased when the cell diameter was greater than 5 mm, and 5 mm diameter katharometer cells are therefore preferred.

Changes in cell diameter did not have any significant effect on the degree of separation.

4. *Effect of metal cell walls*—The sensitivity of a straight wire katharometer cell was not changed by using a metal cell, i.e. 5 mm diameter stainless steel tube (1 mm wall thickness) fitted with glass ends to support the platinum wire. A spiral platinum wire katharometer might be improved in this way since the metal walls should reduce the high internal wall temperatures. However, this has not been tested because of constructional difficulties.

5. *Effect of wire gauge*—For a given current, the sensitivity was increased by reducing the diameter of the platinum wire, due to the increase in wire temperature, e.g. the sensitivity with 48 s.w.g. wire was about four times greater than 44 s.w.g. wire. However, with a given voltage supply, more current will pass through a thicker wire and this will reduce the difference in sensitivity between the wires of different diameter. In fact, with a 6 V supply to the bridge there was little difference in sensitivity between wires of 44 and 48 s.w.g. In practice we find it more convenient to use 44 s.w.g. platinum wire because the katharometers are more easily constructed from the thicker wire and are more robust. So far no satisfactory way has been found for employing longer than 10 cm lengths of wire without increasing the volume of the cell or using a spiral form of wire.

All katharometer cells exhibit a certain amount of instability, i.e. 'noise' which ultimately limits the sensitivity that can be obtained by increasing the wire temperature. Some of the 'noise' is due to pressure fluctuations and vibrations affecting the rate of loss of heat from platinum wire, and thinner wires might be expected to be more susceptible to this effect. No significant difference was observed, however, in the stabilities of the 44 and 48 s.w.g. wire katharometers provided the wires were sealed into the glass envelopes under slight tension.

Part II. Combustion to carbon dioxide

For this work a silica combustion chamber of about 10 ml capacity was introduced between the end of the chromatograph column and the katharometer

cell. The effect of a copper oxide filling, heated to about 700 C, and of a platinized asbestos filling heated to about 900 C was studied.

Extremely large negative peaks, obtained after ignition over platinized asbestos, were attributed to formation of carbon monoxide due to incomplete oxidation; this was prevented by using oxygen as the carrier gas, but satisfactory conditions were not found for obtaining reproducible peak heights.

Satisfactory results were obtained on C_8–C_{11} alcohols, with copper oxide as oxidizing agent (and air as carrier gas); a considerable increase in sensitivity (see *Table I*) was obtained provided water was removed from the combustion

Table I

Condition	*Ambient temperature for katharometer* °C	*Octanol peak height* (mV *deflection* per mg *octanol*)
Combustion chamber removed, i.e. zone measured as octanol	160	4
With CuO *combustion chamber, water not removed by Anhydrone*	27	8
With CuO *combustion chamber, water removed by Anhydrone*	160	4·5
	27	15

products (by means of a small Anhydrone drying tube placed after the ignition chamber) and the ambient katharometer temperature was that of the room.

The increase in sensitivity, will, of course, depend on the carbon content of the compound.

The degree of separation of the C_8–C_{14} alcohols was not significantly altered by the combustion despite the presence of the combustion chamber and drying tube which might have been expected to allow some mixing.

The reproducibility of peak heights was found not to be inferior to normal vapour phase chromatographic measurements provided a short interval of time was allowed between each experiment for the copper oxide packing to be re-oxidized.

Satisfactory analyses of chloro- and nitrochloro- compounds have not been obtained because of interaction of the halogen and the copper to give a volatile copper salt which blocked the exit from the ignition chamber.

Part III. Column efficiency

For this work the thermal conductivity of the emergent zones was measured directly to avoid any chance of zone-mixing which might occur in the carbon dioxide combustion apparatus. The mixtures examined were specially selected (see below) because hitherto their separation efficiency [calculated as number of theoretical plates (t.p.)[3]] had been small or as with a mixture of *o*- and *p*-xylene the separation efficiency had been large but complete resolution had still been found difficult on a 3 ft column.

1. *Flow rate*—The effect of flow rate was observed in the separation of dichlorobenzene and trichlorobenzene on a 3 ft Celite/silicone grease column at 160 C, and of *o*- and *p*-xylene on a 3 ft Celite/dinonyl phthalate column at 75°C [*Figures 2* and *3*(a)].

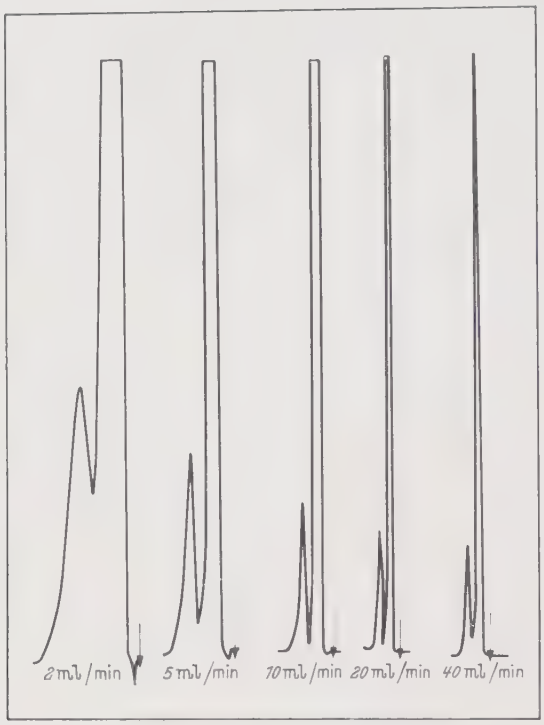

Figure 2. Effect of flow rate on separation of dichlorobenzene (90 per cent) *and trichlorobenzene* (10 per cent). 3 ft × 8 mm *column Celite/silicone grease.*
Exit pressure 5 cm *of mercury; load* 0·04 ml*; column temperature* 160°C

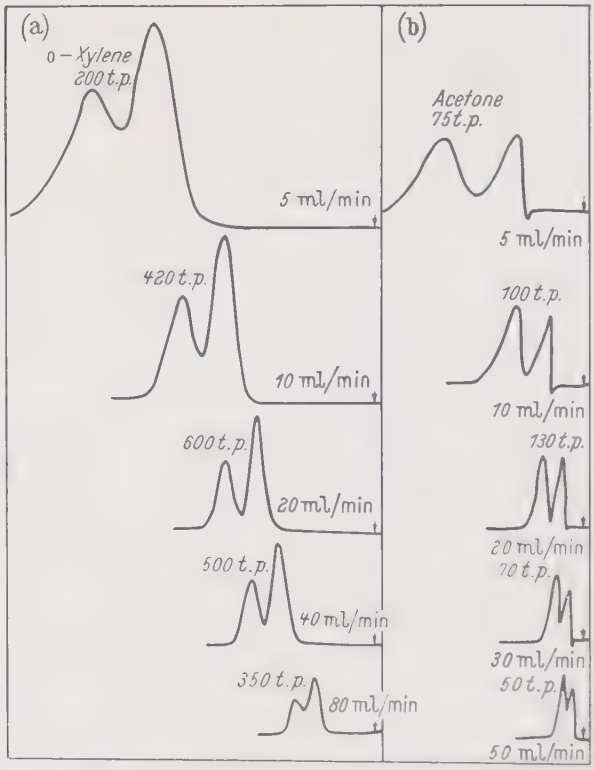

Figure 3. Effect of flow rate on separation: (a) *separation of* o- *and* p-*xylene* (1:1) *in* 3 ft *Celite/dinonyl phthalate column* (75°C). *Outlet pressure* 5 cm *of mercury; load* 0·02 ml. (b) *Separation of acetone and methanol* (1:1) *on* 3 ft *Celite/dinonyl phthalate column* (75°C). *Applied inlet pressure; atmospheric pressure at outlet; load* 0·04 ml

The column efficiency varied with carrier gas flow rate and a fairly critical flow rate was found which gave best resolution. This critical flow rate (20–30 ml air at 760 mm of mercury/minute for an 8 mm diameter Celite column) was found to be independent of column temperature, pressure, column length and load size, and depended only upon the diameter of the column and the particle size of the filling.

Experiments with methanol/acetone mixtures on 3 ft and 9 ft long columns packed with Celite/dinonyl phthalate showed that this critical flow rate value was independent of column length, as in *Table II*.

Table II

Flow rate ml/min	5	10	20	40
Number of theoretical plates:				
on 3 ft *column* (27°C)	25	40	80	50
on 9 ft *column* (50°C)	120	180	220	200

The efficiency of the experiments is given for convenience as the number of theoretical plates calculated on the acetone zone because the effect of flow rate on the 9 ft column was not readily observed on the conductance records due to the components being completely separated at each flow rate tried. The same critical flow rate was found using applied pressure at the inlet, with atmospheric pressure at the outlet [*Figure 3*(b)].

The effect of flow rate was studied with mixtures of *o*- and *p*-xylenes on 4, 8 and 16 mm diameter columns, and the critical flow rate was found to be proportional to the area of cross section of the column (*Figure 4*). The load

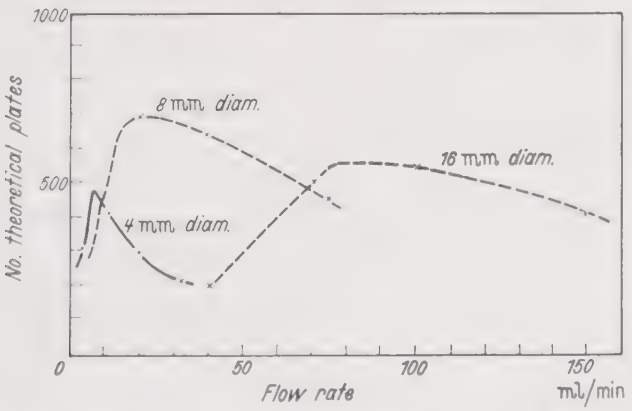

Figure 4. Effect of flow rate and column diameter on column efficiency (calc. on o-xylene)

volumes used in these experiments were proportional to the column area with the exception of the 4 mm diameter column, i.e. 16 mm diameter, load 0·08 ml; 8 mm diameter, 0·02 ml; 4 mm diameter, 0·01 ml. The relatively greater load used on the narrow column accounts for the lower efficiency.

Similar work carried out on columns packed with silicone grease supported on coarse Celite prepared from Celite 205 (30–60 mesh) and salt[1] (30–60 mesh)

showed that the critical flow rate on such coarse fillings is about 5 ml/min for an 8 mm diameter column.

Retention volumes have been defined[1] as the product of the flow rate and the appearance time of the centre of the peak. Since these values depend upon the inlet and outlet pressures of the column, changes in flow rate produce changes in the retention volumes. These changes are very great for separations carried out at low outlet pressures.

Chromatographic peaks are not always perfectly symmetrical; often the rear slope is less sharp than the front, although the reverse has been observed with several compounds. The symmetry was found to be influenced by flow rate and tailing zones could be made more symmetrical by increasing the flow rate. In general the most symmetrical peaks were obtained at the critical flow rate but even where this was not so (e.g. acetone gives a tailing zone, benzylidine acetone gives a diffuse front and sharp tail) the best separations of these compounds from other closely boiling compounds have been obtained at the critical flow rate.

In the determination of trace amounts of a fast travelling component which is easily separated from other components of greater retention volume, it was found advantageous to use a flow rate slower than the critical value in order to increase the detection sensitivity.

2. *Effect of pressure*—Better separation of methanol/acetone mixtures was obtained using applied inlet pressure (atmospheric pressure at the outlet) than with reduced outlet pressure. In these experiments the column temperatures were adjusted to give identical retention volumes at the same flow rate, see *Table III*.

Table III

Condition	*No. of theoretical plates*
Column temperature 75 C, *applied pressure at inlet*, 76 cm *of mercury at outlet*	130
Column temperature 27°C, *reduced pressure at outlet* (5 cm *of mercury*)	80

This effect was also observed with trichlorobenzene/dichlorobenzene mixtures although the improvement with applied pressure here was not as marked.

The object of working under reduced pressure is to allow lower column temperatures to be used so that the technique can be extended to higher boiling mixtures, and also to reduce the possibility of thermal degradation. Since the effect of pressure changes on separation is not as significant as other factors, e.g. column temperature, column length, we have found it more convenient to use reduced pressure for the separation of all mixtures having boiling points greater than about 100°C.

3. *Effect of column temperature*—The efficiency of a vapour phase column was found to be considerably affected by changes in temperature; separations were improved by lowering the temperature (*Figure 5*), which increased the

retention volume of the zones and also caused the zones to broaden. There is possibly a limit to the increase in resolving power which can be obtained by lowering the temperature, i.e. when the zones broaden at the same rate as the retention volumes increase, but with the separations examined the efficiency improved even down to temperatures below the boiling points of the mixture components. However, at the lower temperatures, the time required for a

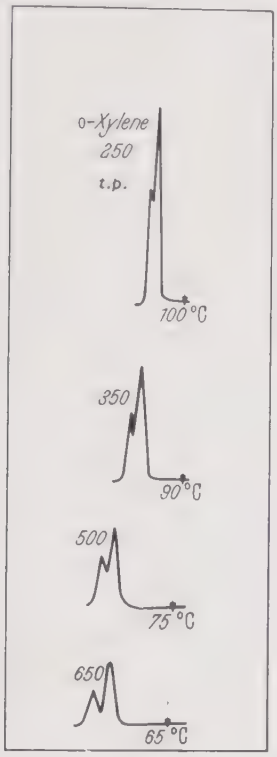

Figure 5. Effect of column temperature on the separation of o- *and* p-*xylenes on* 3 ft *Celite/silicone grease column. Exit pressure* 5 cm *of mercury; flow rate* 20 ml/min*; load* 0·02 ml

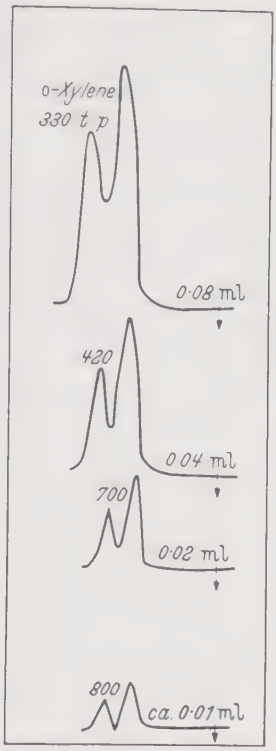

Figure 6. Effect of load size on the separation of o- *and* p-*xylenes on* 3 ft *Celite/dinonyl phthalate column* (80°C). *Exit pressure* 5 cm *of mercury; flow rate* 25 ml/min

separation becomes excessive, and the zones become too diffuse for useful analysis. The chromatographic peaks usually became more symmetrical as the temperature was reduced; the peak heights were also decreased, so that it was necessary when determining trace components to work at the highest temperature which gave a complete separation.

4. *Effect of column diameter and load size*—The most efficient flow rate was found to be proportional to the area of the column [Part III(1)] and provided this flow rate was used, wider columns could be employed, with proportionately greater loads, without much loss in efficiency.

The degree of separation on a given column may be dependent on the load size, when better separations are obtained with smaller loads (*Figure 6*). This effect normally occurs only with major components on columns which are being overloaded; when the load size is reduced so that a linear peak height/concentration relationship is obtained, little if any improvement in

separation is obtained by further reduction in load size. In our experience the most satisfactory column diameter for general analytical work is 8 mm. which allows measurable sample loads to be used, e.g. 0·02–0·05 ml.

5. *Effect of column length*—Experiments with acetone/methanol mixtures on 3 ft and 9 ft long columns at the same temperature, outlet pressure and flow rate showed that the increased efficiency obtained on the longer column was relatively greater than the increase in length (*Figure 7*). The pressure

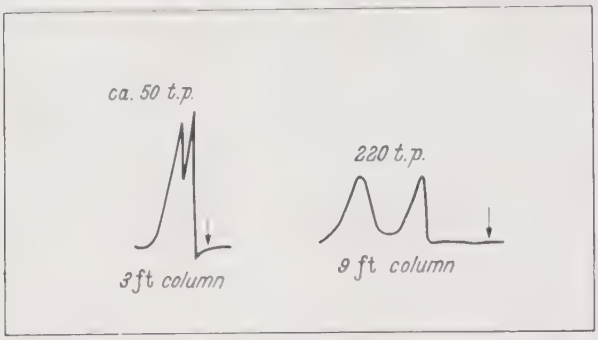

Figure 7. Effect of column length on separation of methanol/acetone (1:1). *Column temperature* 50°C; *outlet pressure* 5 cm *of mercury; flow rate* 20 ml/min (760 mm *of mercury*)

drop through a column increases with length and therefore retention volumes are not proportional to column length. This fact probably accounts for the separations on the longer column being rather better than expected.

The improvement in separation was only partly due to the increased retention volume of the mixture because separations were still superior on the longer column when the column temperatures were adjusted to give identical retention volumes (at constant flow rate), e.g. 3 ft column at 27°C = 80 t.p.; 9 ft column at 75°C ≡ 170 t.p.

Columns 3 ft long were found satisfactory for many analytical problems, efficiencies of 400–500 t.p. generally being obtained on Celite fillings. More difficult separations are carried out on 9 ft and 15 ft columns which are made compact by folding into 3 ft parallel lengths so that they fit conveniently into a 3 ft electric furnace.

6. *Effect of particle size*—The effect of particle size was studied with a dichlorobenzene and trichlorobenzene mixture and the column temperatures were adjusted to give approximately equal retention times at the critical flow rates.

The efficiency of a column was reduced by increasing the particle size of the static phase support, as in *Table IV*.

Table IV

Condition	*No. of theoretical plates*
(1) *Coarse Celite, prepared from Celite 205,* (30–60 *B.S.S.)/silicone grease at* 90°C	110
(2) *Salt* (30–60 *B.S.S.)/silicone grease at* 90°C	100
(3) *Fine Celite 545/silicone grease at* 120°C	250

Since coarse fillings (together with low pressure) allow separations to be carried out at lower temperatures they have been found essential for mixtures which are decomposed by high temperatures[1]. It is possible, however, that the same effect could be obtained by using shorter column lengths of the Celite 545 support.

Conclusions

(*1*) Katharometers should be maintained at as low a temperature as possible provided that there is no risk of condensation; a straight 44 s.w.g. platinum wire is recommended, and if maximum sensitivity is required the wire current should be as high as possible provided that 'reversal' in sensitivity is not caused thereby. 5 mm diameter glass cells are satisfactory.

(*2*) Increased sensitivity can be obtained by combustion over copper oxide, removal of water by Anhydrone, and detection of carbon dioxide by a katharometer held at laboratory temperature; the increase in sensitivity arises largely from the fact that the katharometer ambient temperature can be kept low. Combustion to carbon dioxide would probably only be worth while when very small amounts of impurities are being detected or measured, and we have not as yet found it necessary in our work.

(*3*) The separation efficiency on a given column is best at the critical flow rate, which depends only on column diameter and particle size of static phase; increased diameter has little effect on separation provided that flow rate and load are adjusted proportionally to the area of cross section of the column; increased particle size reduced the separation efficiency. An 8 mm diameter column is recommended for analytical work.

(*4*) At the critical flow rate, separation efficiency is better: (*a*) at lower column temperatures, but the retention volumes eventually become too great and the zones too broad; (*b*) when the load is kept below the level at which the column becomes 'overloaded' (i.e. below the level above which peak height does not vary linearly with concentration); (*c*) with longer columns, but 3 ft columns are adequate for most problems which we have encountered; (*d*) with applied inlet pressure rather than reduced outlet pressure (with Celite 545 support); however, it is more convenient to use reduced pressure with the relatively higher boiling samples, and it is essential to use it when there is a tendency for thermal decomposition to occur.

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Note: For Discussion see pages 81 86, where Chapters 6 and 7 are treated together.

7

FACTORS AFFECTING THERMAL CONDUCTIVITY DETECTORS IN VAPOUR PHASE PARTITION CHROMATOGRAPHY

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The behaviour of the thermal conductivity detector is more dependent on such operating variables as the temperature of the wire and the wall of the cell than had previously been thought. Besides previously known abnormalities that arise through dissociation of dimeric molecules on the hot wire, there are changes in the conductivity of one gas relative to another, and in mixtures the thermal conductivities are not necessarily additive. Examples are given demonstrating the behaviour of mixtures of nitrogen with various vapours, such as methanol, methylamine, hexane, acetic acid and benzene.

These observations indicate that care must be taken in choosing the correct hot wire current and wall temperature of thermal gas analysers in this connection and have a bearing on the selection of the optimum working pressure in any analysis. A few observations are included on the effect of the diameter of the cell.

Most varieties of vapour phase chromatographic apparatus depend upon a hot-wire or thermistor for detection and determination of the separated fractions. The sensitivity of these devices is a function of the thermal conductivity of the mixture of fraction vapour and carrier gas at the moment of observation. In some conditions, as the observations described below showed, the thermal conductivity changes in an unexpected way. Serious errors can arise if this possibility is not borne in mind. It is incorrect to regard thermal conductivity in these circumstances as a specific molecular property strictly proportional to concentration.

In the course of some analytical separations of mixtures containing methanol it was observed that a katharometer working with a platinum wire temperature in the region of 100 C was less sensitive to methanol than when the wire was at 60 C. Further investigation showed that raising or lowering the temperature around the 100 C level could result in the thermal conductivity of a nitrogen–methanol mixture becoming either greater or less than that of pure nitrogen.

It had previously been observed by Lambert, Staines and Wood[1] during an investigation into the thermal conductivities of some organic vapours that the behaviour of methanol is anomalous. The variation of thermal conductivity with pressure was investigated by these authors for a number of organic vapours at pressures between 50 and 700 mm of mercury and at temperatures of 25, 66 and 85 C. It was found that acetaldehyde and acetonitrile show

fairly large linear increases of thermal conductivity with rise in pressure, the pressure coefficient diminishing markedly as temperature rises: this is interpreted as being due to reversible dimerization.

Benzene, *cyclo*hexane, *n*-hexane, chloroform and diethyl ether, together with air and carbon dioxide, all show comparatively small linear pressure dependence, which becomes larger as temperature rises.

Methanol and acetone behaved differently in showing a linear increase with pressure, the magnitude of which diminished at higher temperatures, and which was interpreted as being due to association to polymers higher than the dimer.

These observations showed that anomalies were to be expected in chromatographic analysis with thermal detectors and it was decided to make further investigation into the phenomena.

Experimental

The katharometer used in our investigations was of the standard Billingham type and consists of a large metal block through which are drilled two holes 13 mm in diameter to form the cells through which pass 0·001 inch diameter platinum wires arranged axially, each wire having a resistance of about 25 ohms.

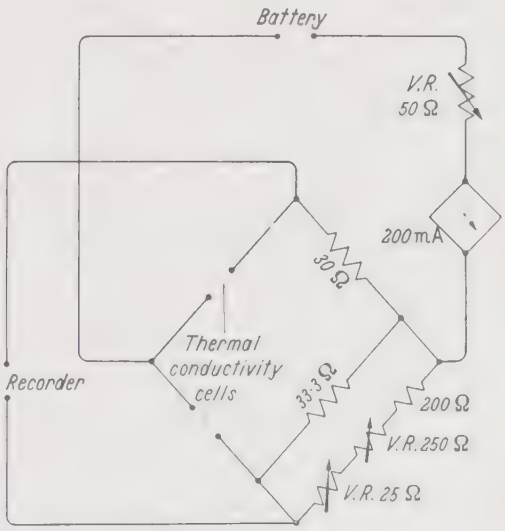

Figure 1. Bridge circuit for vapour phase chromatography

The cells form two arms of the Wheatstone bridge network shown in *Figure 1*, current to the bridge being supplied by a 6 V accumulator. Out-of-balance e.m.f. is measured on a 15 mV full scale deflection Sunvic recorder.

Saturated nitrogen–methanol mixtures were prepared in the following convenient manner. A small glass vessel 3 to 4 inches deep and 2 inches in diameter was packed with ungraded Celite 545 impregnated with methanol, and maintained at the requisite temperature. Nitrogen passed through the bed of impregnated Celite at 5 l./h is accurately saturated with methanol.

Results

Various nitrogen–methanol mixtures were prepared by varying the temperature of the saturator between 0–20 C: the resulting methanol concentrations were between 3 and 12·5 % v/v. The mixture was passed through one

Table I. Katharometer Temperature = ca. 20°C

Methanol conc. % v/v	*Deflection* mV	*Katharometer bridge current* mA	*Katharometer pressure*
3·9	0·5	100	
3·9	1·5	150	
3·9	2·6	200	
7·25	0·8	100	
7·25	2·5	150	1 atm.
7·25	4·6	200	
12·5	1·1	100	
12·5	3·7	150	
12·5	7·3	200	
3·9	0·5	100	
3·9	1·5	150	
3·9	2·8	200	
7·25	0·9	100	
7·25	2·7	150	200 mm Hg
7·25	5·0	200	
12·5	1·3	100	
12·5	4·4	150	
12·5	7·6	200	

Table II. Katharometer Temperature = 100°C

Methanol conc. % v/v	*Deflection* mV	*Katharometer bridge current* mA	*Katharometer pressure*
3·9	0·10	100	
3·9	0·17	150	
3·9	−0·17	190	
7·25	0·25	100	
7·25	0·43	150	1 atm.
7·25	−0·08	190	
12·5	0·42	100	
12·5	0·83	150	
12·5	0·25	190	
3·9	0·13	100	
3·9	0·13	150	
3·9	−0·17	190	
7·25	0·23	100	
7·25	0·40	150	200 mm Hg
7·25	0·0	190	
12·5	0·50	100	
12·5	1·00	150	
12·5	0·50	190	

cell of the katharometer while a constant stream of pure nitrogen passed through the other.

The effects of varying the rate, bridge current and katharometer block temperature upon the out-of-balance voltage were investigated at three methanol concentrations. The pressure in the katharometer was maintained either at 1 atmosphere or at 200 mm of mercury in different series of experiments.

In *Table I* are presented the out-of-balance voltages obtained when the block was at room temperature and in *Table II* the corresponding values when the block was heated to 100°C.

Review

It may be seen from *Table I* that changing the pressure of the gas mixture in the katharometer from 1 atmosphere to 200 mm of mercury has little effect on the recorder deflection. (This is contrary to the effect observed by Lambert and his co-workers but it is to be remembered his measurements were made upon pure vapour.) It was also observed that flow rate had no appreciable effect upon the recorder deflection.

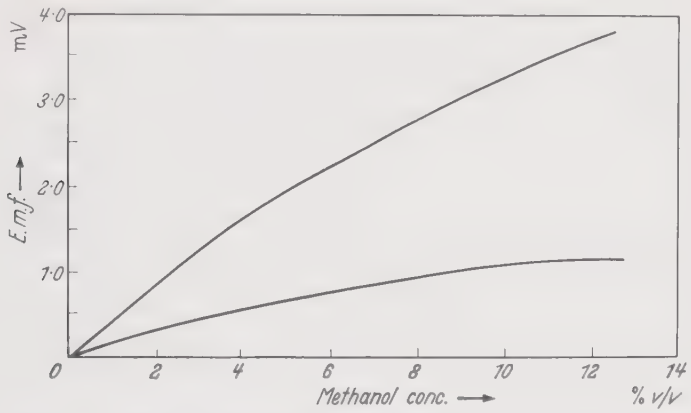

Figure 2. Recorder deflection as a function of methanol concentration

The variation of recorder deflection with methanol concentration is shown in *Figure 2* for two wire temperatures corresponding to bridge currents of 100 and 150 mA (see later) and with the katharometer block at room temperature in both cases. It is evident that the quantitative sensitivity of the katharometer varies considerably with the wire temperature and with the methanol concentration but in a regular way.

On increasing the katharometer block temperature to 100°C, however (*Table II*), deflections are very much less and increase of bridge current from 150 to 190 mA in all cases resulted in a decreased deflection. The observed thermal conductivity of methanol at high temperatures is nearly equal to that of nitrogen and in some cases reversal with respect to pure nitrogen occurs over a fairly narrow range of conditions.

Effect of wire temperature

The actual temperatures of the katharometer wire at the bridge currents used for the above work were next determined, published data having suggested

that temperatures in excess of 200°C would raise the thermal conductivity of methanol above that of nitrogen.

The thermal conductivities of the mixtures under examination were calculated as follows:

Nitrogen (No temperature range given). Dickens[2]

$$K_0 = 58{\cdot}1 \times 10^{-6} \text{ g. cal. cm}^{-1} \text{ sec}^{-1} (\text{C}^\circ)^{-1} \text{ at } 0^\circ\text{C}$$

$$a = 29 \times 10^{-4}$$

$$K_t = K_0(1 + at)$$

Methanol 20 to 130°C. Shushpanov[3]

$$K_0 = 32{\cdot}7 \times 10^{-6} \text{ g. cal. cm}^{-1} \text{ sec}^{-1} (\text{C}^\circ)^{-1} \text{ at } 0^\circ\text{C}$$

$$A = 0{\cdot}155, \quad B = 5 \times 10^{-4}$$

$$K_t = K_0 + AT + BT^2$$

The conductivities of nitrogen and of methanol calculated from the above data at 100C° intervals from 0 to 400°C are given in *Table III*.

Table III. Conductivities of Nitrogen and of Methanol

Temperature °C	0	100	200	300	400
Nitrogen	58×10^{-6}	75×10^{-6}	92×10^{-6}	109×10^{-6}	126×10^{-6}
Methanol	$32{\cdot}7 \times 10^{-6}$	53×10^{-6}	84×10^{-6}	123×10^{-6}	174×10^{-6}

In *Figure 3* are plotted the wire temperatures calculated from measured wire resistance at 0°C and the known temperature coefficient for 0·001 inch diameter platinum wire.

As it appeared that the thermal conductivity of methanol–nitrogen mixtures approaches that of nitrogen more rapidly than would be expected, it was decided to explore the possibility of a maximum in the thermal conductivity/composition curve of these mixtures, such maxima having previously been reported for carbon monoxide and carbon dioxide by Ishikawa and Yagi[4] and by Rothman and Bromley[5].

One cell of the katharometer was therefore replaced by a resistance box and as the values of the other resistances were known the resistance of the hot katharometer wire and the current passing through it could be calculated. The temperature of the wire being known by reference to *Figure 3* and the measured block temperature also being known, an approximate thermal conductivity could be calculated from the equation

$$Q = [2\pi Kl(t_1 - t_2)/\ln (r_2/r_1)] + S$$

where Q = heat dissipated per second, l = length of wire, t_1 and t_2 = wire and block temperatures, r_1 and r_2 = wire and cell radii, and S = heat loss due to radiation (assumed negligible).

Thermal conductivity/composition curves for nitrogen–methanol mixtures were determined at wire temperatures between 60 and 160°C and are plotted in *Figure 4* over a range of 0–20% v/v methanol in nitrogen.

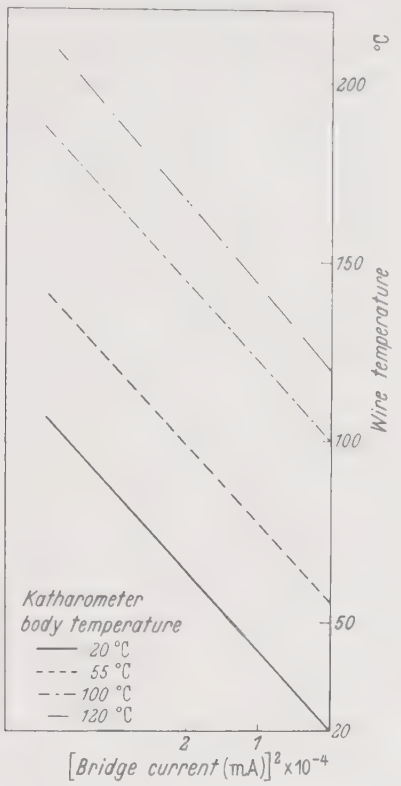

Figure 3. Variation of katharometer wire temperature with current

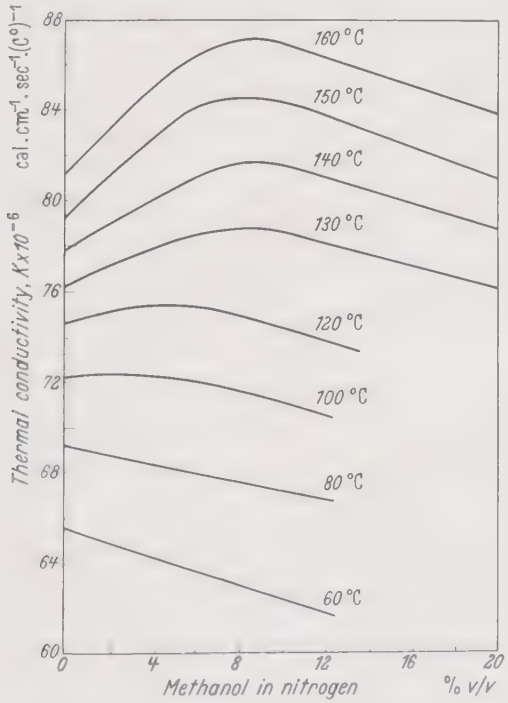

Figure 4. Thermal conductivity of methanol–nitrogen mixtures

The results of our experimental determinations for a 12·5% v/v methanol–nitrogen mixture gave a thermal conductivity equal to that of nitrogen at a temperature of between 120 and 130°C.

Our experiments concluded with a series of determinations of the thermal conductivities of 1·0% v/v mixtures of benzene, toluene and ethylbenzene at a number of differing bridge currents with katharometer body temperatures of 60 and 100°C respectively. The recorder deflections obtained are contained in *Table IV*.

Table IV

Katharometer body temp.	*Bridge current* mA	*Recorder deflections* mV		
		Benzene	*Toluene*	*Ethylbenzene*
60°C	100	0·34	0·44	0·50
	125	0·66	0·78	0·96
	150	1·08	1·28	1·56
	175	1·58	1·80	2·36
	200	2·24	2·44	2·76
100°C	100	0·26	0·34	0·32
	125	0·46	0·64	0·70
	150	0·76	1·04	1·10
	175	1·14	1·28	1·68
	200	1·50	1·80	2·18

The effect of operating temperature on sensitivity is evident, but there is no indication with these hydrocarbon vapours of the reversal of conductivity with respect to nitrogen which was observed with the methanol mixtures.

Survey

The curves in *Figure 4* exhibit well defined maxima which increase with rising temperature. At wire temperatures of 160°C and at low concentrations of methanol the katharometer is very sensitive to changes in concentration. The conductivity values are greater than that of pure nitrogen and a katharometer operated at this temperature would give rise to 'negative' peaks on a chromatographic elution plot obtained in the normal manner with nitrogen as eluant gas.

For analytical purposes the concentrations measured in the katharometer are rarely greater than 2% v/v and it may be seen that over the range 0–2% methanol in nitrogen the katharometer sensitivity changes by a factor of 5 if the wire temperature changes from 130 to 160°C. The wire temperature will change with changes in either the current through it or the katharometer block temperature.

Further consideration of *Figure 4* shows that at wire temperatures around 100°C the maximum flattens considerably and that the portion of the curve covering the 0–2% range is almost parallel to the horizontal axis: at this temperature the katharometer is insensitive to concentration changes.

Below 100°C the initial portion of the curve slopes towards the horizontal

axis: katharometer wires operated below this temperature will give the normal 'positive' methanol elution peaks.

It is suggested by Lambert and his co-workers that organic vapours may be roughly divided into two types with respect to their thermal conductivity behaviour, and that polar compounds would behave like methanol. In corroboration of this we have been able, in the progress of analytical separations, to produce a similar reversal of elution peak with such substances as the lower aliphatic acids (C_1 C_4), some phenols, ammonia and mono- and di-methylamine.

Conclusions

The results described in the foregoing show that:

(1) Reversal of the elution peak for a polar organic liquid may result from a change in the operating temperature of the thermal conductivity cell.
(2) If the cell wire temperature is chosen incorrectly then loss of sensitivity or even complete insensitivity to a particular substance may result.
(3) For non-polar substances unnecessarily high cell wire temperatures will give rise to low sensitivity.
(4) In order to obtain maximum sensitivity and resolution from this type of detector, the inclusion of the katharometer in the column heating chamber should be avoided. If heating of the katharometer body becomes necessary to prevent condensation then independent heating should be provided.

References

[1] Lambert, J. D., Staines, E. N. and Woods, S. D. *Proc. Roy. Soc.* **200**, 262, 1950
[2] Dickins, B. G. *Proc. Roy. Soc.* **143**, 517, 1934
[3] Shushpanov, P. I. *J. exp. theor. Phys.* **9**, 875, 1939
[4] Ishikawa, F. and Yagi, K. *Bull. Inst. phys. chem. Res. Japan* **22**, 12, 1943
[5] Rothman, A. J. and Bromley, L. A. *Industr. Engng Chem. (Industr.)* **47**, 899, 1955

DISCUSSION

Note: Chapters 6 and 7 are treated together.

C. S. G. Phillips: Before opening the discussion this afternoon I should like to announce that a small committee has been nominated to make some definite recommendations about nomenclature and presentation of results. The members are Drs Martin, James, Keulemans, Glueckauf, Mr Desty and myself. The committee will meet this evening and make its recommendations at the end of the meeting. Those of you who have contributions to make on the way results should be expressed, or on standardization should do so as early as possible in the meeting, preferably this afternoon, when there is a convenient opportunity because some of the papers are in fact concerned with this point.

G. Dijkstra: Considering the wide use of the katharometer, measurements like those described by Mr Harvey are of prime importance. I should like to stress however, that extreme caution is necessary in the interpretation of results. *Figure 7* on page 230 shows that at higher temperatures in the low concentration range the thermal conductivity of methanol seems to start above that of nitrogen, falling rapidly below it with increasing concentration. I should like to put the question to Mr Harvey as to whether he has found evidence for this too.

As we have found that this peak inversion is independent of the temperature of the main mass of gas, being solely dependent on the wire temperature, we must either assume that this wire temperature is the temperature at which we are

measuring thermal conductivity, or that other thermal effects occur on the wire surface. The fact that increasing amounts of aldehyde were found in the outcoming gas with increasing peak inversion effects in alcohols points to dehydrogenation taking place on the wire. This would cool down the wire in accordance with observation. Also, *cyclo*hexane, being in the non-polar class of substances, shows a peak inversion, so that for this substance Lambert's classification would not apply.

The decrease of the inversion effect with increasing cell diameters, as reported by Mellor, would be explained by the drowning of the decomposition effect by increasing importance of the thermal conductivity of the larger amount of gas. The increase in the effect when spiral wires are used can also be explained by decomposition effects on the hot spots inside the spiral.

Although thermal conductivities of gas mixtures certainly do not vary linearly with composition, this is not the only effect involved in these thermal conductivity measurements and there are hidden traps even in these careful investigations.

F. M. Ebeid: I have found that using high bridge current and high column temperature, factors that lead to high sensitivity, could also cause the decomposition of peroxides that may be present in a combustion product to be analysed. Therefore the output of the bridge was fed, not directly to a recorder, but to an amplifier. A high sensitivity was obtained using this technique while the total bridge current was only 80–100 mA.

C. W. Munday: Mr Mellor's experience that wider tubes in the katharometer give greater sensitivity is contrary to our experience in measuring thermal conductivity of gases such as air.

If the diameter of the katharometer cell is reduced the heat transfer rate from the wire to the cell surface for a given wire temperature is increased. A greater wire current and higher bridge voltage can be used without any increase in wire temperature. The increase in sensitivity noted by Mr Mellor is probably due to chemical reactions taking place on the wire.

N. H. Ray: It was found when using a wide-bore thermal conductivity cell of about 10 c.c. internal volume, that three peaks could sometimes be obtained when only two components were present. This was observed particularly with ethanol/ethyl acetate mixtures in the region of equal molar concentrations, when a third peak was found to appear between the alcohol and ester peaks. This spurious peak disappeared completely when the volume of the thermal conductivity cell was reduced to about 3 c.c. Although the explanation of this effect is not known to the contributor, it is perhaps important to point out the danger of interpreting curious results obtained in large thermal conductivity cells.

G. R. Primavesi: I would like to ask Mr Mellor just what he means by his last sentence in the paper. It says, 'It is essential to use it when there is a tendency for thermal decomposition to occur'.

I cannot see why reducing the pressure at the outlet should enable the column to be run at a lower temperature (page 70, para. 2). The concentration of the solute vapour depends only on its vapour pressure over its solution in the stationary phase and not on the pressure of the carrier gas, which is well above the vapour pressure even for the lowest pressures quoted.

Also unless there is a sudden reduction at the outlet of the column, reducing the outlet pressure cannot prevent condensation in the katharometer.

In connection with Mr Harvey's paper the concentrations given in *Figures 2* and *4* are mainly much higher than would be encountered in practice. The curves are substantially linear over the relevant portions (up to about 4 per cent) and all the results mean is that the katharometer must be calibrated for each substance at each temperature.

G. O. Morgan: With reference to the last statement made by the last speaker, we are quite aware that we never obtain concentrations up to 15 per cent, and it

would have been really quite sufficient to determine thermal conductivities up to 4 per cent. However, the plot does not look very convincing, so we did a few more concentrations just to show what did happen and why the effect of adding small quantities of ethanol was to reverse the direction.

N. Mellor: In reply to Mr Munday we realize the need to keep the katharometer cell volume as low as possible when detecting trace components but we find under the conditions used in our apparatus that with major zones the sensitivity of the cell is increased by increasing the cell diameter from 1·5–9 mm. In practice we compromise on 5 mm diameter cells.

In reply to Mr Primavesi we find that having the column under reduced pressure allows lower column temperatures to be used without increasing the retention time.

G. F. Harrison: The effect of wire temperature on katharometer sensitivity, described by the two speakers, has been confirmed in our laboratory.

Two examples of temperature/sensitivity curves are given in *Figure 9* on page 342.

The output of the detector bridge depends not only on the sensitivity of the wire but also on the span voltage. The sensitivity of a katharometer wire was determined at increasing temperatures. A correction was then applied to eliminate the effect of the increased span voltages which were necessary to attain the higher temperatures. It was then found that the sensitivity/temperature curve had a maximum—for the katharometer tested at about 120 C. Above this wire temperature the sensitivity of the katharometer dropped off, but the output from the bridge continued to rise slightly due to the increased span voltage.

G. Dijkstra: I would just like to disagree with the main point which Mr Primavesi and Mr Morgan agreed, that is that these high concentrations are never reached. If you want to measure a series of alcohols and you work at a high temperature, let us say 170°C or something like that, you may well obtain a concentration of about 12 per cent in the middle of the peak for the lower members.

D. Harvey: First, the question was asked, why run at low pressure? I think that the katharometer is insensitive to pressure changes. The effect, then, of reducing the total overall pressure is to increase the concentration of components in the mixture and hence the peak is enhanced and the sensitivity also.

Secondly I would like to discuss the effect of variation in cell diameter when using platinum-in-glass cells. These were all constructed with a 50 gauge platinum wire 10 cm long placed in a glass envelope of about the same length. Cell diameters ranged from 2–10 mm. When operated on a mixture of *iso*octane and nitrogen containing 1·8 per cent of hydrocarbon by volume, the sensitivity showed a maximum against diameter at about 5 mm.

G. F. Oldham: I would like to query Mr Mellor's remark that high-boiling solutes are eluted at lower temperatures if lower exit pressures of carrier gas are used. Were identical linear flow rates of carrier gas used? If so, this implies that the vapour pressure of a solute over the solvent at a given temperature is not independent of the carrier gas pressure, whereas this is always assumed in theoretical treatments. Is not this apparent faster elution due entirely to the increased linear velocity of carrier gas flow as the pressure drop across the column is increased?

A. Heywood: I normally work on these high-boiling problems. It seems reasonable to assume that if you have a reduced pressure on the output you have, consequently, a much reduced pressure on the input of the column, and I think most people do fractional distillations at a reduced pressure. Consequently, we normally do an analysis of stearic acid in which the main body issues in 15 minutes. A recently published paper shows the analysis of this carried out at the same temperature but under atmospheric output conditions, where the time taken was 100 minutes. We are an industrial concern and it is of prime importance that we get our analyses out very quickly. I think you will agree that 15 minutes is preferable to 100 minutes.

C. S. G. PHILLIPS: I think this point has been made. Would either Dr Martin or Dr Keulemans like to sum it up? I think we might well go on all the afternoon about this.

A. I. M. KEULEMANS: There may be various good reasons for applying low column pressures, one being that the concentration of the solutes in the exit gas will be increased, which may give rise to a larger signal from the detector (for instance when thermal conductivity is used as the detection method).

It should, however, be observed that the rate of transport of solute bands through the chromatograph column is a function of the linear velocity of the carrier gas and independent of the pressure of the carrier gas. In the first paper by James and Martin this fact has been emphasized. In this paper it was also mentioned that the linear velocity is determined by the difference of inlet and outlet pressures rather than by their ratio.

From the point of view of column efficiency it can be said that low column pressures generally adversely affect the separation. Anticipating the paper to be presented by Cropper and Heywood I should like to draw attention to *Figure 4*(a) (page 324). The number of plate equivalents estimated for the arachidate peak is roughly 20, which means that the HETP is about 50 mm, whereas an HETP below 2 mm can readily be obtained. In my opinion the low efficiency of the Cropper and Heywood column must be ascribed for a great part to the low column pressures.

É. R. ADLARD: There appears to be some confusion on this subject. One must distinguish between effects on the column and effects on the thermal conductivity cell.

As far as the column is concerned the effect of working at low pressures is to reduce the efficiency, due to the increase in gas velocity down the column. However, as can be seen from *Figure 4* on page 20, the drop in efficiency with increasing gas velocity is small if the pressure drop across the column is not too big. It is an important practical advantage to have the inlet of the column below atmospheric pressure since this facilitates both introduction and rapid vaporization of the sample. Rapid vaporization is essential to ensure maximum column efficiency.

Consider now the effect of pressure on the katharometer. The effect of reducing the carrier gas pressure is to increase the *concentration* of the organic vapours in the gas stream as they pass through the katharometer. Therefore a bigger signal is obtained for a given quantity of a substance present in the original mixture. Secondly, it is an experimental fact that reduction in pressure enables the katharometer temperature to be lowered considerably without the risk of condensation. My opinion is that this may be due to the high gas velocity through the katharometer—the vapour does not have time to condense or, if it does, it is swept away almost immediately. Whatever the reason, this ability to reduce the katharometer temperature is important, since it minimizes the possibility of thermal decomposition and (with nitrogen as carrier gas) usually effects a further increase in sensitivity.

A. J. P. MARTIN: The last speaker said that at low pressure the higher rate of flow prevents condensation in the katharometer. I feel this is quite impossible.

As to the apparent increase in sensitivity of the katharometer at lower pressures this is a function of the R_F value. If we consider oxygen in nitrogen then reduction of pressure down the column will not change the proportion, since $R_F = 1$, and both expand equally. If the R_F value is less than unity the zone will widen less than the expansion of the carrier gas, widening in proportion to the ratio change of pressure times R_F value; the proportion then increases, due to this pressure drop, by $(p_1/p_0)(1 - R_F)$.

A. F. WILLIAMS: From the practical point of view we chose the most suitable temperature to give the best degree of separation for a given mixture with the column inlet pressure above atmospheric. Then in order to obtain the best resolution and sharpness of peaks to make a quantitative analysis, we changed the flow rate to a

suitable value by adjustment of the outlet pressure of the column to the appropriate value below atmospheric. This method of adjustment of flow rate was found to be necessary when very long columns (with a high back pressure) were in use.

D. SPENCER: It is evident that there are several ways of arranging the flow of carrier gas flow through a gas–liquid partition chromatography apparatus and I would be interested to hear views expressed on the following cases when thermal conductivity cells are used for detection:

(*a*) Vacuum applied at outlet of detector cell and gas flow controlled by restriction at GLPC tube inlet.

(*b*) Atmospheric pressure at inlet, vacuum at detector cell outlet and flow controlled by restriction between detector and GLPC tube.

(*c*) Super-atmospheric pressure applied at GLPC tube inlet and gas flow passing through a rate-controlling restriction at the outlet into a detector cell operating at atmospheric or sub-atmospheric pressure.

I consider that operation of a GLPC column under the conditions of case (*c*), where column pressure drop may be small compared with the total operating pressure, and approximately constant linear gas velocity is obtained, might well be expected to give higher efficiencies and more easily reproducible results.

C. M. DREW: In answer to Dr Spencer's question concerning the various arrangements of pressurizing the column and using a vacuum on the outlet, we have tried most of these methods and the last method is the one that we are employing now. With it you can run the column at a series of pressures and find out something about the effect of total pressure on the column with the constant pressure drop over the entire column. We have found no great difference in going from, say, essentially atmospheric pressure up to 100 lb/in^2.

F. VAN DER CRAATS: As broadening of the bands partly depends on the diffusion velocity of the carrier gas, the pressure must have an influence on the plate number of a column.

For a column of internal diameter 6 mm filled with 30 per cent by weight *n*-hexadecane on Sterchamol, 50–80 mesh, the plate number was determined with C_2 and C_3 hydrocarbons at different gas velocities and pressures.

Pressure	*Optimum linear gas velocity*	*Minimum HETP* (see page 24)
1 atm abs.	1·4 cm/sec	1·9 mm
10 atm abs.	0·4 cm/sec	1·2 mm

At 10 atm and a gas velocity of 1·4 cm/sec the HETP was 1·9 mm, viz., the same as for 1 atm.

At elevated pressure a better separation can be obtained, provided also that the gas velocity is adapted to the lower diffusion velocity of the gas.

C. M. DREW: I forgot to mention that we are programming the column pressures as we drive materials over the column and the various constituents coming off the column appear at a given temperature and do not depend on the retention volumes. This may clarify the point raised by Mr van der Craats on the effect of pressure.

R. P. W. SCOTT: A recent speaker mentioned using inlet column pressures, I believe of 10 atmospheres or 140 lb/in^2. We have gone up to 35 lb/in^2 and, as a matter of interest, I would particularly like people working on column efficiency to give an opinion as to the best way in which to use high pressure on inlets. You can do it in two ways, either by using densely packed columns of short length, when you can obtain sometimes a 10 : 1 ratio of plate efficiency per unit length, or you can use it to force a reasonable gas flow through very long columns.

C. H. BOSANQUET: There has been much discussion of the improvement obtainable by running at high pressures and so reducing diffusion. At constant throughput

the time is increased as much as the diffusion coefficient is reduced, this product remains constant and the length of the transition region should be unchanged.

Another point raised was whether high pressure could be employed usefully to force gas through a short tightly packed column and a long loosely packed one. At the optimum rate dynamical diffusion predominates over molecular diffusion and for dynamical diffusion and geometrically similar packings the ratio of length of transition region to column length depends on the ratio of grain diameter of packing to column length. For constant values of this ratio the throughput at constant pressure is proportional to grain diameter so that a long column with coarse packing appears the better proposition provided sample quantity is not limited.

8

MICRO VAPOUR PHASE CHROMATOGRAPHY—EFFECT OF COLUMN TEMPERATURE

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For the application of gas–liquid partition chromatography to the qualitative microanalysis of the complex mixtures of products encountered in kinetic studies, it is suggested that relative, rather than absolute, elution times (proportional to retention volumes) are a more reliable criterion for the characterization of a compound. Elution times of a number of compounds from dinonyl phthalate, relative to that of *n*-pentane arbitrarily chosen as a standard, are correlated as functions of temperature. The effects of changes in some other column parameters have been investigated and a comparison is given of the efficiency of a number of column liquids.

In recent years the techniques of gas–liquid partition chromatography (GLPC) have received increasingly more attention from various workers[1–7]. In particular, a description has been given of the application of this method to the qualitative and quantitative analysis of the higher boiling products from kinetic studies in the gas phase[8,9]. To be of practical value in this connection, it is desirable that a systematic correlation of elution times (which are proportional to retention volumes) be available. Moreover, the techniques and correlations must be shown to be applicable to samples as small as a fraction to a few micromoles.

Previous workers have tended to emphasize the correlation of the elution time of a particular compound with the position it occupies in its homologous series[1,4–6]. Relationships of this type are of considerable value in correlating the increments of elution time with the molecular structure. Further extensions of this approach will undoubtedly be forthcoming. However, the relationships between the partition coefficients and molecular properties of solvents and solutes are complex, and it is, therefore, felt that at present a direct empirical correlation would be more useful for application to kinetic investigations. This is particularly relevant since the products encountered in kinetic studies are frequently composed of widely different types of compounds, not belonging to a single homologous series.

The trend has been to report elution times at a single column temperature for successive members of a series[1]. As a matter of convenience, the temperature chosen has been different, in general, for each series. We have found,

however, in common with other workers, a marked effect of temperature both on the separation efficiency and absolute elution times. Littlewood, Phillips and Price[5] have measured the temperature coefficients of 'corrected retention volumes per gram' (V'_g) for a number of compounds. Determination of these quantities involves a number of auxiliary measurements in addition to that of the elution times. In order to eliminate a number of multiplicative correction factors, we have found it more convenient to express the data in terms of relative elution times (corrected for the 'dead times' only). The relative elution times for a given liquid phase are found to be independent of all the variable conditions investigated and should prove useful in direct systematic qualitative analysis.

Experimental

A general description of the apparatus and the procedure employed has been given before[8]. The techniques for sample introduction, elution, the recording of the 'peaks' and the trapping out of the eluted components of a mixture were such as to make possible a satisfactory analysis of samples of the order of a fraction to several micromoles. The main features incorporated were: (*1*) use of hydrogen as the eluent gas, maintained at ambient pressure at the inlet of the column and at a constant pressure of 30–40 mm of mercury at the outlet; (*2*) introduction of the sample by condensing it into a U-trap near the inlet to the column and injecting it into the eluent gas stream by sudden vaporization; (*3*) detecting the components of the sample in the eluent gas by means of a thermal conductivity cell placed at the outlet of the column and a similar reference cell, placed also *after* the column, the two being separated by a series of liquid nitrogen traps used to condense individually different compounds present; (*4*) use of a d. c. amplifier (Liston–Becker Model 14) and a pen recorder for the off-balance signal from the Wheatstone bridge incorporating the two thermal conductivity cells. This arrangement has proved very satisfactory for the analysis of extremely small samples. The use of hydrogen as the eluent gas instead of nitrogen improves the sensitivity of detection. The placement of both thermal conductivity cells at the outlet of the column, i.e. at the low pressure side, results in an increased stability of the analyser since the relative pressure fluctuations between the two cells are reduced to a very low level. The maintenance of a relatively low pressure at the outlet of the column facilitates a quantitative condensation of the components of the sample. The individual components are thus available for direct manometric measurement or confirmatory analysis by other means when this is necessary.

In the original arrangement the pressure at the outlet of the column was maintained constant by means of a capillary leak and a large buffer volume preceding the vacuum oil pump. Equally stable performance has been obtained by the use of a Cartesian diver type manostat and a relatively small buffer volume. With the use of the manostat the initial stabilization periods are considerably shortened.

The two columns used for most of the present work were: (*1*) 1 part dinonyl phthalate (DNP) and 25 parts glass beads passing 270 mesh and (*2*) 20 parts of Celite 545 and 9 parts of DNP, both tightly packed in two 4-mm internal diameter capillaries 180 cm long. The flow rates in cm^3 (s.t.p.) per minute were, approximately, 1·8 and 15·3, respectively[8].

Carefully degassed research grade chemicals were used. The temperature of the column was held constant to within 1C° by manually adjusting the current through the heating wire.

Results

Elution times were measured on the DNP on glass column at various column temperatures by introducing samples containing three to four compounds at a time. Total sample sizes were five to ten micromoles. In a number of instances the relative elution times were cross-checked by interchanging individual compounds in the samples. The initial times were recorded at the

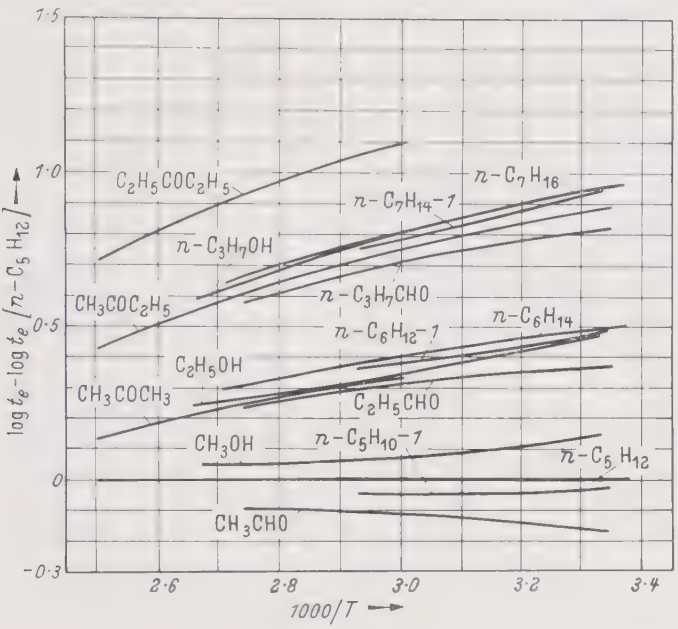

Figure 1. Relative elution times from DNP

time of vaporization of the samples by momentarily altering the resistance in the variable arm of the Wheatstone bridge. The uncorrected elution times (t_u) corresponded to the peak maxima. The only correction subsequently applied was for the 'dead volume' of the apparatus. This was done in a manner similar to that employed by Littlewood, Phillips and Price[5] by introducing into the samples a trace of a substance virtually insoluble in DNP. Usually the samples already contained a trace of low boiling impurity and the 'dead times' recorded in this manner coincided with the peaks produced by such substances as carbon dioxide, nitrous oxide or air. From each recorded time of a peak maximum the corresponding dead-time was subtracted to obtain the elution time (t_r). The logarithms of the relative elution time (q), taking t_r for *n*-pentane under identical conditions as unity, are plotted for all the substances investigated against $1000/T$ (see *Figure 1*). The choice of *n*-pentane as a reference is purely arbitrary and the common logarithms of the relative elution times for any two substances can be read easily from the vertical separation of the corresponding curves in *Figure 1* at any $1000/T$ value. The plots in *Figure 1* represent the best smooth curves

through the experimental points. To avoid congesting the figure the experimental points are not shown; most of the relevant experimental measurements are listed instead in *Table I.*

In order to show that the relative elution times are independent of the supporting material in the column, a mixture of *n*-pentene-1, *n*-hexene-1, and *n*-heptene-1 was chromatographed on the two columns, with DNP supported on glass beads and Celite respectively. In addition to the difference in the

Table I. Elution Times at Different Column Temperatures (DNP on glass beads)

Column temp. °C	t_u min	t_e min	log *q*	t_u min	t_e min	log *q*	t_u min	t_e min	log *q*
	n-C_5H_{12}			*n*-C_6H_{14}			*n*-C_7H_{16}		
24	14·1	11·1	—	38·2	35·2	0·501	108·8	105·8	0·979
25	13·8	10·8	—	36·9	33·9	0·497	103·2	100·2	0·967
47	9·2	6·2	—	20·2	17·2	0·443	49·1	46·1	0·871
50	8·9	5·9	—	18·8	15·8	0·428	44·6	41·6	0·848
68	7·2	4.2	—	13·3	10·3	0·390	29·2	26·2	0·795
77	6·8	3·8	—	11·5	8·5	0·350	23·8	20·8	0·738
96	6·2	3·2	—	9·4	6·4	0·301	17·3	14·3	0·650
	CH_3CHO			C_2H_5CHO			*n*-C_3H_7CHO		
26	10·05	7·05	0·170	27·4	24·4	0·369	73·6	70·6	0·831
35	8·8	5·8	0·152	21·8	18·8	0·354	54·3	51·3	0·795
51·7	7·1	4·1	0·140	14·75	11·75	0·326	33·25	30·25	0·737
70	6·3	3·3	0·088	11·3	8·3	0·309	22·6	19·6	0·684
92	5·6	2·6	0·087	8·55	5·55	0·240	15·1	12·1	0·579
92	5·6	2·6	0·089	8·55	5·55	0·240	15·45	12·45	0·591
	CH_3OH			C_2H_5OH			*n*-C_3H_7OH		
27	17·2	14·2	0·149	33·0	30·0	0·473	96·5	93·5	0·967
39	12·6	9·6	0·113	22·6	19·6	0·423	60·1	57·1	0·910
49	10·2	7·2	0·085	17·2	14·2	0·380	42·5	39·5	0·856
76	7·3	4·3	0·056	10·6	7·6	0·303	21·7	18·7	0·694
102	6·6	3·6	0·075	8·4	5·4	0·251	15·1	12·1	0·602
	CH_3COCH_3			$CH_3COC_2H_5$			$C_2H_5COC_2H_5$		
60	13·2	10·2	0·331	29·35	26·35	0·743	64·4	61·4	1·110
75	10·15	7·15	0·272	20·4	17·4	0·659	42·15	39·15	1·011
90·5	8·95	5·95	0·259	16·55	13·55	0·616	32·2	29·2	0·949
104	7·95	4·95	0·216	13·7	10·7	0·550	24·95	21·95	0·862
127	6·7	3·7	0·137	10·3	7·3	0·432	17·2	14·2	0·721
	n-C_5H_{10}-1			*n*-C_6H_{12}-1			*n*-C_7H_{14}-1		
26	13·7	10·5	0·019	36·7	33·5	0·485	103·8	100·6	0·963
28	12·8	9·6	0·032	34·2	31·0	0·477	94·7	91·5	0·947
39	10·5	7·0	0·049	24·2	20·7	0·422	61·1	57·6	0·866
50·2	8·9	5·5	0·044	18·9	15·4	0·404	44·7	41·2	0·831
68·7	7·2	4·0	0·040	13·4	10·2	0·367	28·3	25·1	0·758

supporting material, the flow rates and the total amounts of the liquid phase were vastly different in the two cases. As a result of the larger flow rate and the greater amount of DNP the dead-time in the Celite column was considerably smaller. The results are given in *Table II* and it is shown that the relative

Table II. Comparison of Relative Elution Times for Olefins on the Glass and the Celite Supported DNP Columns

Column temp. °C	*Type of column*	*Dead-time* min	*n*-C_5H_{10}-1		*n*-C_6H_{12}-1		*n*-C_7H_{14}-1		$\log \frac{t_e[n\text{-}C_6H_{12}\text{-}1]}{t_e[n\text{-}C_5H_{10}\text{-}1]}$	$\log \frac{t_e[n\text{-}C_7H_{14}\text{-}1]}{t_e[n\text{-}C_5H_{10}\text{-}1]}$
			t_u min	t_e min	t_u min	t_e min	t_u min	t_e min		
26	*glass*	3·2	13·7	10·5	36·7	33·5	103·8	100·6	0·504	0·981
26	*Celite*	0·8	9·3	8·5	28·1	27·3	82·5	81·7	0·507	0·983
39	*glass*	3·5	10·5	7·0	24·2	20·7	61·1	57·6	0·471	0·915
39	*Celite*	0·8	7·0	6·2	19·2	18·4	52·4	51·6	0·472	0·920
68·5	*glass*	3·2	7·2	4·0	13·4	10·2	28·3	25·1	0·407	0·798
68·5	*Celite*	0·8	3·5	2·7	7·6	6·8	17·5	16·7	0·401	0·791

elution times are the same for the two columns at the three different temperatures investigated. The fact that relative elution times are independent of flow rates has been further checked on a single column by direct flow rate variations over a factor of about five.

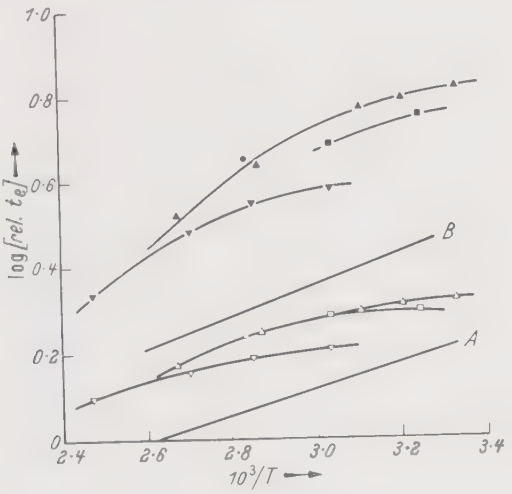

Figure 2. Comparison of elution times from several column liquids

	C_2H_5OH/CH_3OH	$n\text{-}C_3H_7OH/CH_3OH$
Silicone 702 (ref. 5)	□	■
Tritolyl phosphate (ref. 5)	▽	▼
Dinonyl phthalate (ref. 4)	○	●
Dinonyl phthalate (this work)	△	▲
Triethylene glycol (this work)	*line A*	*line B*

The relative elution times shown in *Figure 1* should be reproduced on any DNP column. It is possible to make an approximate comparison of some of the data reported here with the results of Ray[4] who used a DNP column under conditions considerably different from those employed here. While no numerical data are reported, it is possible to obtain approximate uncorrected times for recording peak maxima by direct measurement of *Figure 2* of that

work. The logarithms of this time, relative to that of the lowest member of the series, are shown in *Table III* along with values interpolated from the present work. In all cases the agreement is rather poorer than might be anticipated, even in view of the crude method of measuring the literature

Table III. Comparison of Elution Times from DNP with Literature Data

		log (*relative elution time*)		
Column temp. °C	*Compounds*	*Ray*[4]		*This work*
		Uncorr.	*Corr.*	
65	n-C_6H_{14}/n-C_5H_{12}	0·27	0·41	0·38
	n-C_7H_{16}/n-C_5H_{12}	0·58	0·78	0·78
	n-C_7H_{16}/n-C_6H_{14}	0·31	0·37	0·40
80	CH_3COCH_3/CH_3CHO	0·22	0·40	0·37
	$CH_3COC_2H_5$/CH_3CHO	0·54	0·84	0·79
	$CH_3COC_2H_5$/CH_3COCH_3	0·32	0·44	0·41
80	C_2H_5OH/CH_3OH	0·24	—	0·24
	n-C_3H_7OH/CH_3OH	0·66	—	0·66
	n-C_3H_7OH/C_2H_5OH	0·42	—	0·42

values. By assuming that $t_r[n\text{-}C_7H_{14}]/t_r[n\text{-}C_5H_{12}]$ is correctly given in the present work, a calculated dead-time is obtained from Ray's data of 2·2 min. (This dead-time gives more consistent agreement than others which may be calculated.) Using this value, the corrected results in the table are obtained. It is seen that agreement to within 0·03 logarithm units is achieved in this fashion. The carbonyl compounds shown in *Table III* have been corrected with the same dead-time; after this correction is made a reasonable agreement is again achieved. The similar ratios of the aliphatic alcohols, also shown in *Table III*, are in excellent agreement with the ratios obtained here. This agreement is consistent with the assumption that, in this last case, the dead-times were negligibly small, possibly due to the altered conditions.

The ratios of elution times, with a few exceptions, increase as the column temperature is lowered. Nevertheless, there is considerable overlapping of peaks of compounds belonging to different homologous series at all temperatures suitable for DNP columns. It is, therefore, of interest to compare the data for columns with various liquid phases. The available experimental information is as yet somewhat limited. Our own experiments with a column packed with triethylene glycol (~30 per cent) on Celite 545 showed that the paraffin mixture (n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}) is not resolved even at room temperature. The lower aliphatic alcohols showed large elution times, but the actual separation factors are smaller than those obtained on DNP at the same temperature. Similarly, a column using stopcock grease as the immobile

phase (~1 per cent Apiezon T on glass) gave no resolution for paraffins, olefins or alcohols, although some separation of the lower ethers was achieved at room temperature.

Elution times for the series of normal aliphatic alcohols (methanol, ethanol and *n*-propanol) are reported in the literature[1,5] for a number of liquid phases at various temperatures. In *Figure 2* these data, together with some of our own, have been plotted as log (relative elution time) versus

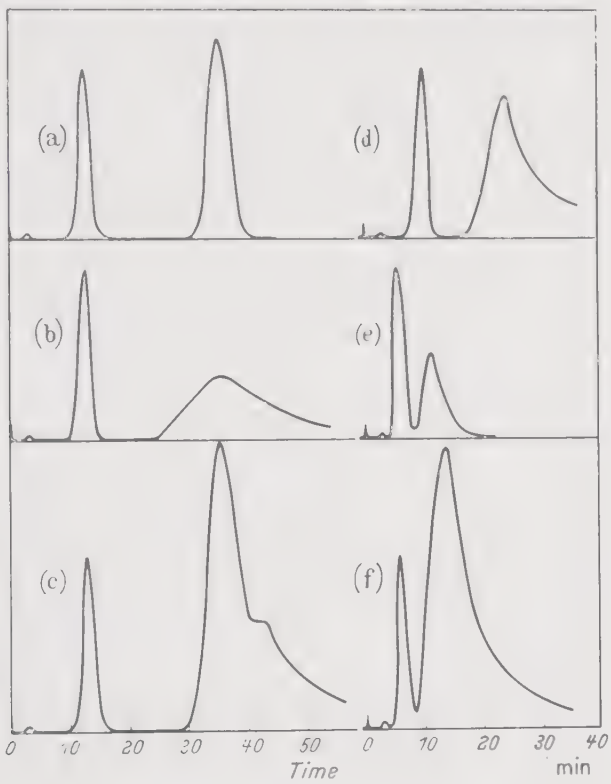

Figure 3. Elution of water from DNP on glass beads. In all cases the first peak represents 0·8 micromoles (μM) *of* n–C_5H_{12}

In addition the samples contained:
(a) 1·8 μM n-C_6H_{14} (*column temp.* 25°C)
(b) 21 μM H_2O (*column temp.* 25°C)
(c) 1·8 μM n-C_6H_{14}, 22 μM H_2O (*column temp.* 25°C)
(d) 18 μM H_2O (*column temp.* 39°C)
(e) 7 μM H_2O (*column temp.* 88°C)
(f) 24 μM H_2O (*column temp.* 88°C)

reciprocal temperature, taking $t_r[CH_3OH] = 1$. Experimental points have been omitted from the triethylene glycol plot, the best fit lines only being reported. For this particular homologous series the general trends on different liquid phases are similar, although there is a considerable variation in the values of separation factors. It is to be hoped that accumulation of data on relative elution times on various columns will suggest specific advantages which can be gained in particular cases by a change of liquid phase.

Several determinations have been made with water on a DNP on glass column in an attempt to establish its relative elution time. It has been observed before[8] that water is not recovered quantitatively from a DNP column. We find that water exhibits in general an irregular peak with a very

gradual and prolonged tailing. This is especially pronounced at lower column temperatures. Quantities of one to two micromoles as a rule do not produce peaks. Several micromoles result in a relatively low, but broad and deformed peak. At a column temperature of around 90 C the peaks are considerably more pronounced but still exhibit appreciable tailing. Working with quantities from several to about 20 micromoles we find that the positions of the maxima of the irregular water peaks vary somewhat with the amount used. The relative elution time curve for water would roughly coincide with that of *n*-hexane in *Figure 1*. The irregular shapes of the water peak might be explained by an overloading of the column by the relatively large amounts which must be used in order to obtain the peaks. This is, however, unlikely since similar and larger amounts of other substances behave normally. It is possible that the initial vaporization of water into the stream of the carrier gas is slower than that of the other substances. Moreover, in view of the observed incomplete recovery of water, it appears that some irreversible (or slowly reversible) adsorption takes place. Either of these latter two effects could result in peaks of the general shape exhibited by water. As shown in *Figure 3* (a), (b) and (c) the presence of relatively large amounts of water does not affect the peak of *n*-pentane, which precedes it, and appears to provide only an altered background for the peak of *n*-hexane, which largely coincides with it. In *Figure 3* are also shown the characteristic peaks of water obtained at 25, 39 and 88°C, as well as the shift in peak maximum with larger samples [*Figure 3*, (e) and (f)].

Review

The plots in *Figure 1* give information on the *ratios* of the elution times for different compounds but not the actual *resolution* of the peaks. Whenever the logarithmic separation of the plots in *Figure 1* for two compounds is quite small a smaller or greater overlapping or even complete merging of peaks takes place. While the ratio of the elution times for two solutes is constant for a given liquid phase and column temperature, the resolution depends on the resolving power (customarily expressed as the number of theoretical plates) of the particular column used. The theoretical aspects of peak resolution have been treated by Glueckauf[10] and by James and Martin[1]. They show that

$$N = 8(t_e/\beta)^2$$

where N is the number of theoretical plates of the column, t_e the elution time and β the peak breadth (expressed in the same units as t_e) at $1/e$ of the peak height. In an approximate manner we can consider that two peaks are essentially completely resolved when $t_{e_2} - t_{e_1} \geq \beta_1 + \beta_2$. Taking $t_{e_2} > t_{e_1}$ and writing $q = t_{e_2}/t_{e_1}$, and $\alpha = (N/8)^{1/2}$, it is readily seen that the minimum value of q for complete resolution is $q_r = (\alpha + 1)/(\alpha - 1)$, provided the number of theoretical plates of the column remains the same for the two compounds. Thus when $N = 1000$, $q_r = 1{\cdot}20$ and $\log q_r = 0{\cdot}08$. Approximately when

$$\tfrac{1}{2}(\beta_1 + \beta_2) < (t_{e_2} - t_{e_1}) < (\beta_1 + \beta_2)$$

the presence of two peaks (and their location) is discernible in spite of partial overlapping. When $t_{e_2} - t_{e_1} = \frac{1}{2}(\beta_1 + \beta_2)$, the ratio of the elution times

becomes $q_m = (2\alpha + 1)/(2\alpha - 1)$. When $N = 1000$, $\log q_m = 0{\cdot}04$, so that peaks merge for logarithmic separations smaller than 0·04, partially overlap between 0·04 and 0·08, and are completely resolved for separations greater than 0·08 logarithm units. The common logarithm plots of q_r and q_m for various values of N are given in *Figure 4*. Similar information concerning q_r

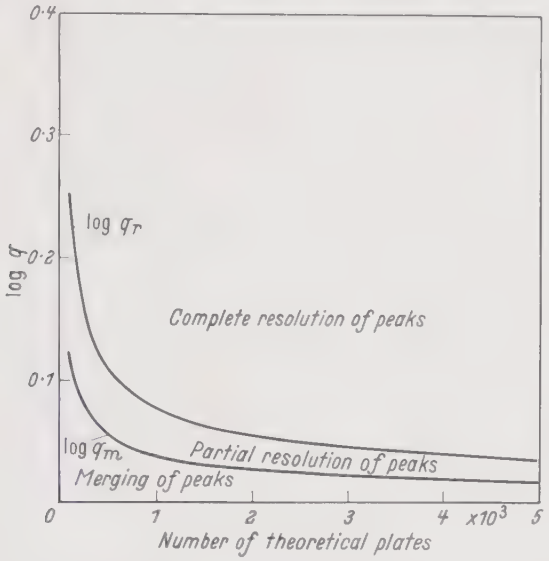

Figure 4. Peak resolution as a function of the number of theoretical plates

can be obtained from Fig. 3 of Glueckauf's work, assuming impurity fractions of about 10^{-3}. The delineation of the three regions must be considered approximate, since ideal (error curve) peaks and constant N for the two compounds are assumed. In particular, for lighter compounds the broadening of peaks due to diffusion in the gas phase may become quite appreciable and result in an apparent low N and consequently low resolution.

The plots in *Figure 1* exhibit slight curvatures and the tangents at various values of $1000/T$, which are determined by the differences in heats of solution, have, in general, finite intercepts at $1000/T = 0$. This is consistent with the previous findings of other workers that the heats of solutions of gases are not independent of temperature. An assumed linear variation of the heats of solution with temperature leads to the empirical relationship for gas–liquid partition coefficients, and therefore also for the relative elution times, of the form

$$\log q = a/T + b \log T + c$$

Some of the curves in *Figure 1* have been tested and found to be readily adaptable to this empirical equation. No attempt was made, however, to determine the constants a, b, and c, for the different compounds plotted since for the present purpose the direct graphical presentation appears to be much more convenient.

A systematic characterization of various compounds can be made in terms of their corrected retention volumes per gramme in the manner suggested by Littlewood, Phillips and Price[5]. For chromatographic microanalysis, where samples of the order of a fraction to several micromoles are encountered, the

maintenance of low outlet pressures offers distinct advantages. Under these conditions accurate flow rate determinations would involve considerable difficulty so that the correlation of the corrected retention volumes per gramme obtained by different workers would be uncertain. It appears, therefore, that the characterization of different compounds by their relative elution times from a given column liquid, a possibility also considered by these authors, is both more convenient and more reliable.

The authors are indebted to Mr L. C. Doyle for assistance with the measurements reported in this work.

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DISCUSSION

C. M. Drew: Why is it necessary to use reduced pressure on the column exit in order to achieve good recovery? We make successful recovery with atmospheric pressure using helium carrier gas.

K. O. Kutschke: In reply to Mr Drew, I can only state that our experience has been less successful than theirs. Small differences in apparatus and techniques could account for this, but we have been unsuccessful in obtaining complete trapping using an atmospheric outlet whereas with lower outlet pressures recoveries are within experimental error of 100 per cent.

F. van der Craats: In connection with freezing out fractions, on rapid cooling of a mixture of a carrier gas and a condensable vapour, the formation of fog or minute crystals often occurs.

Without using filters a good recovery can be obtained by placing several cooling traps in series and heating the gas stream between the individual traps sufficiently to evaporate the floating droplets or crystals again.

With a very simple construction, as described by H. de Vries, *Appl. sci. Res., Hague*, *B***5**, 387, 1956, a recovery of more than 99 per cent was obtained in condensing 0·1–1·0 mg fractions of C_2-hydrocarbons. The trap consists of 5 mm glass tubing bent into three hairpins each of 40 cm length the lower part of which (10 cm) is cooled in liquid nitrogen.

G. J. Minkoff: I would like to make a couple of suggestions perhaps if I could speak on a slightly wider aspect of this committee which is meeting tonight. The first point is with regard to the journals in which we publish our results. At the moment there is a wide choice of places where one finds information and, as there are more and more people in different fields, this will get worse and worse. Perhaps the classic example is that Dr Martin's original suggestion of this technique in 1942 was published in the *Biochemical Journal* and I think was obviously not read by a lot of chemists to whom it would have been of interest. I wonder if it would

perhaps be an idea if this committee were to suggest two or three journals to which we might, as far as possible, send most of this information which is going to be of use to other people.

The other suggestion is to consider whether it might be worth while creating an informal discussion group rather on the lines of the spectroscopic and infra-red discussion groups which are quite informal and meet about half a dozen times a year to discuss problems of mutual interest, in which things can be said without their being written down and quoted against them afterwards.

E. GLUECKAUF: It may perhaps be worth while to comment on the collection of very small samples, because it seems that a number of questions on this point are still uncertain.

We found that in a freezing-out trap, if the space is not allowed to be completely open but filled, for instance, with cotton wool or some other material on which droplets can collect, there is a complete condensation up to the vapour pressure of the particular substance concerned. If the vapour pressure of the substance itself should be too high at liquid nitrogen temperature, which does occasionally occur, then the way out of the difficulty is to have a small plug of absorption charcoal. We had no difficulty whatsoever, for instance, in gas chromatographic separations of products such as krypton and xenon in obtaining quantitative retention of materials, which have quite a high pressure, in quantities less than 10^{-12} gramme.

G. F. HARRISON: I would like to make a suggestion for the committee meeting tonight, and that is that there should be some standard way of talking about the sensitivity of the detecting devices we use. We have had in the literature from time to time the claim that something is ten times more sensitive than the katharometer, and it probably is. But I do not know how that value is arrived at. I personally feel that any measurement of sensitivity should be made quite separate and distinct from a column assembly. In other words, the detector should be considered as a detector pure and simple, and the effect of the chromatograph column on a compound and the broadening of a peak ought to be completely eliminated. If that can be put on the agenda for the committee I think we shall all appreciate it very greatly. It will be a very useful topic for consideration later on in the meeting.

9

AN EVALUATION OF SOME POLYGLYCOLS USED AS STATIONARY PHASES FOR GAS-LIQUID PARTITION CHROMATOGRAPHY

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'Shell' Research Limited, Thornton Research Centre

The factors controlling the suitability of a substance for use as a liquid stationary phase in gas-liquid partition chromatography are stated and discussed. Several compounds of the polyglycol type have been examined as stationary liquids, and retention volumes and partition coefficients of many common organic compounds obtained. In the light of the results the utility of these liquid stationary phases for certain types of separation is indicated. The influence which the support for the liquid phase may exert is noted, especially with regard to analysis of mixtures with a high water content.

VARIOUS substances have been recorded in the literature for use as liquid stationary phases in gas-liquid partition chromatography (GLPC) and although James and Martin[1] explained the separations obtained on the basis of the forces acting on the various compounds when in solution, such explanations can only give a broad indication of the separations to be expected from a given liquid. Recently Keulemans, Kwantes and Zaal[2] have applied the theory of solutions to the behaviour of compounds passing through GLPC columns. However, in order to predict the behaviour of substances with respect to a given stationary liquid, it is necessary to know the activity coefficients of the compounds in the liquid. At present, a more empirical approach is capable of giving quicker results. Indeed the process may be reversed and, provided that effects due to the solid carrier can be neglected, the behaviour of compounds on a GLPC column may be used to calculate values of activity coefficients.

James and Martin used a polyethylene-oxide polymer as a stationary liquid[1], but a glance at suppliers' catalogues shows that there are many different compounds available having this type of structure with slight variations. The main types of compounds available are listed below.

1. *Polyethylene glycols* (*PEG's*)

$$HOCH_2CH_2—[O—CH_2CH_2]_n—OCH_2CH_2OH$$

These compounds are available in a range of molecular weights from 106 (diethylene glycol) to 6000 ($n \sim 100$) and above. The physical properties of these substances range from high boiling liquids to hard waxes. The lower members are completely miscible with water: the higher members become less

soluble with increasing molecular weight although they are still very soluble. Their solubility is low in paraffin hydrocarbons and high in aromatics. The reverse of this will probably be true, i.e. that paraffins will have a low solubility and aromatics a high solubility, and this is a factor of some importance with respect to the behaviour of the polyglycols when used as stationary liquids in GLPC.

2. *PEG's with end groups*

$$ROCH_2CH_2—[OCH_2CH_2]_n—OCH_2CH_2OH$$

$$ROCH_2CH_2—[OCH_2CH_2]_n—OCH_2CH_2OR'$$

In this range of materials there is the possibility of an almost infinite number of combinations since, besides the variation in the polyglycol chain length, the end groups can be practically anything which will combine or condense with an alcoholic OH group. The commonest end groups are long chain alcohols or fatty acids which result in ethers and esters, respectively.

3. *Polypropylene glycols (PPG's)*

$$HO—\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2—[O\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2]_n—OCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H—OH$$

These exist in a range of molecular weights similar to the PEG's. In general, they are more soluble in organic solvents and less soluble in water than their PEG equivalents. PPG compounds with end groups are also commercially available though they are less numerous than the PEG types.

4. *Mixed polymers*

Co-polymers and block polymers of ethylene and propylene glycol can be obtained but little information about their exact structure is available.

A few of these different types of polymer have been taken and examined for their utility in GLPC. While the criteria given below will enable the majority of the remainder to be eliminated and the limitations of the rest to be more clearly recognized, the final test for any liquid must be its performance in a column.

Survey

The essential requirements which a liquid must possess in order to be used as a stationary phase for GLPC are listed below. The list is not in order of importance since most of the conditions are inter-related.

(*1*) The liquid must have no definite and irreversible chemical action on the compounds passing through the column. Phosphoric acid has been used in columns containing silicone fluid to assist the separation of fatty acids[3,4], but a mixture of alcohols passed through such a column might be partially dehydrated to give a mixture more complex than the original. On the other hand, the formation of transient adducts may be desirable and permit type separation to be achieved. For example, aromatic hydrocarbons may be partially separated from paraffins on columns containing picric acid[2] presumably because the aromatics form unstable adducts which retard their

progress. It may be a useful artifice to remove certain compounds chemically before they enter the partition column proper, but this technique obviously cannot be classed as GLPC.

(*2*) The liquid must be thermally stable at the desired temperature of operation. Not only must it be stable in bulk but it must remain stable on the solid support – which on occasion has proved to be an excellent catalyst for its decomposition! The calculated vapour pressure[5] of dinonyl phthalate at 140 C is 0·03 mm of mercury and on the basis of this alone it ought to be perfectly satisfactory at this temperature, whereas in actual fact it decomposes quite rapidly at 140°C on Celite.

(*3*) The liquid must have a low vapour pressure, otherwise the separating power of the column will be constantly varying and it will have a very short operating life. This factor is of even greater importance when the apparatus is operated by sucking the gas through the column with a vacuum pump, when outlet pressures as low as 20 mm of mercury may be used. Although it has not been rigorously proved, it would seem probable that the vapour pressure of the liquid to be used as the stationary phase should not exceed 1 mm of mercury at the temperature of operation, otherwise the life of the columns will be too short. PEG 400* has a vapour pressure of 0·15 mm of mercury at 100 C and a column containing this liquid has been operated continuously at this temperature, an outlet pressure of 200 mm of mercury and an inlet flow rate of one litre of nitrogen per hour (at s.t.p.) for 400 hours with little loss in efficiency (*Figures 1* and *2*). Probably substances with vapour pressures of the order of 0·5 mm of mercury and less will give a column life perfectly satisfactory for normal purposes.

It has been suggested that more volatile liquids might be used as stationary phases by saturating the carrier gas with the vapour of the liquid before the gas enters the column. This technique might be useful for large scale work but for small analytical columns using thermal conductivity cells as detectors it is often desirable to have the katharometer at a lower temperature than the column. Trouble would then be experienced due to condensation of the liquid phase in the katharometer, connecting pipes, etc.

(*4*) In order to achieve maximum efficiency the liquid used should have a low viscosity, so that rapid equilibrium is obtained between the gas and liquid phases. This factor does not seem to be of such critical importance as the previous ones since liquids with widely different viscosities give equally effective columns.

(*5*) At least one of the compounds being separated must be fairly soluble in the column liquid, otherwise no separation will take place at all. A good example of this has been given for saturated and aromatic hydrocarbons, and water. The ratio of the solubilities of saturates and aromatics in water is such that, on this basis alone, water would be a very good medium for separating the two types of compound. However, their solubilities in water are both so small that the method has no practical value whatsoever.

For some purposes it is desirable that only one class of compounds should have any appreciable solubility in the stationary liquid or, failing this, all classes except one should be soluble, since in this way type separation is

* The number after the name refers to the average molecular weight of the polymer.

obtained. The analyst is unfortunately seldom presented with a mixture as simple as a homologous series, and it is for this reason that liquids which will give type separation are of great importance.

The PEG's 200, 400, 600 and 1000

These compounds satisfied the first condition for suitability as stationary phases in that they were chemically inert with respect to all the compounds commonly encountered in the author's laboratory. It was thought that the

Figure 1. Ketones and alcohols on a PEG 400 column after 12 h *running at* 100°C. *Number of plates*[6] $= 2\pi(hl/a)^2$ *where* h = *peak height,* l = *retention distance (corrected for dead-space),* a = *peak area. From the* isobutanol *peak: number of plates* $= 2\pi(21{\cdot}35 \times 9{\cdot}35/16{\cdot}0)^2 = 978$

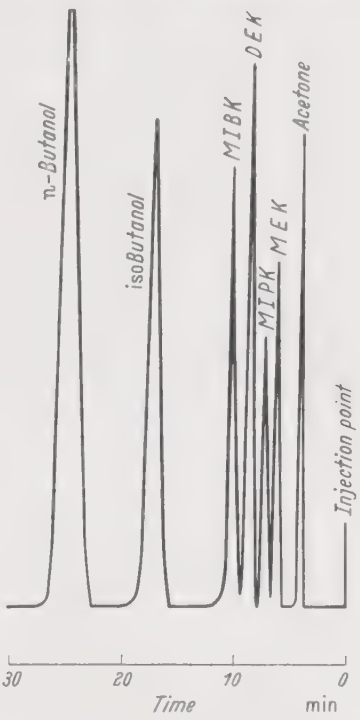

Figure 2. Ketones and alcohols on a PEG 400 column after 400 h *running at* 100°C. *From the* isobutanol *peak: number of plates*
$= 2\pi(21{\cdot}46 \times 8{\cdot}06/14{\cdot}1)^2 = 946$

higher the molecular weight of the PEG the lower the vapour pressure at any given temperature. While this may be true at room temperature, it was found that the higher molecular weight compounds had a poorer thermal stability. Above 100°C the optimum molecular weight from vapour pressure considerations was found to be 400 (*Table I*). However, at 100 C all the PEG's were stable enough for their separatory powers to be compared and for this purpose the limiting retention volume per gramme of stationary liquid (V_g) at 100 C was determined for a number of common organic compounds. The limiting retention volume per gramme of liquid suggested by Phillips, (Littlewood *et al.*[6]), while not being as fundamental as a partition coefficient, is

Table I. Vapour Pressures of Polyglycols

Substance	*Vapour pressure at* 100°C mm Hg	*Temperature for vapour pressure of* 0·5 mm Hg °C	*Temperature for vapour pressure of* 1 mm Hg °C
PEG 200	0·18	115·1	125·8
PEG 400	0·15	123·6	138·3
PEG 600	0·28	108·5	118·9
PEG 1000	0·36	104·5	114·5
Methoxy PEG 350	0·15	119	131
Methoxy PEG 550	0·19	117·1	128·6
PPG 425	0·22	117·3	132·8
PPG 1025	0·47	101·3	116·7

Note: The values given in this table are the vapour pressures of the compounds plus the vapour pressures of their decomposition products.

easier to calculate. V_g values are satisfactory for comparing the behaviour of stationary liquids provided that the same percentage of liquid is used on the inert carrier in each case (see text and *Figure 10*, page 108).

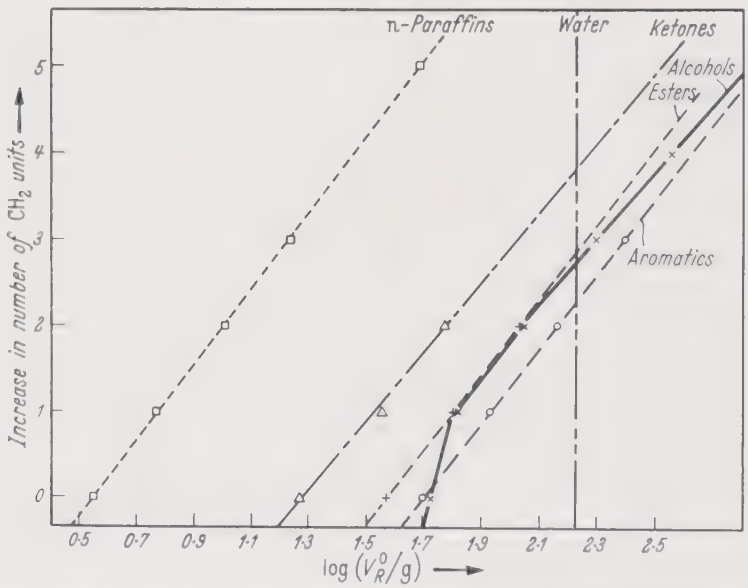

Figure 3. Relation between CH_2 *units and* $\log (V_R^0/g)$ *for various types of compounds on a PEG 400 column at* 100°C

Paraffins: n-*pentane to* n-*decane. Aromatics: benzene, toluene,* m-*xylene, mesitylene. Alcohols: methanol to* n-*amyl alcohol. Ketones: acetone, methylethyl ketone, diethyl ketone. Esters: ethyl acetate to* n-*butyl acetate*

Figure 3 shows a graph of CH_2 units plotted against $\log (V_R^0/g)$ for five series of compounds on a PEG 400 column. It is immediately apparent from this graph that the saturated hydrocarbons are separated from the other types of compound and pass through the column very quickly. *n*-Decane

emerges just before benzene, a boiling point reversal of 94C°. It would seem, therefore, that this liquid would be useful for the determination of alcohols, ketones and esters in saturated hydrocarbon solvent mixtures, and especially useful for the determination of small quantities of aromatics in paraffin mixtures.

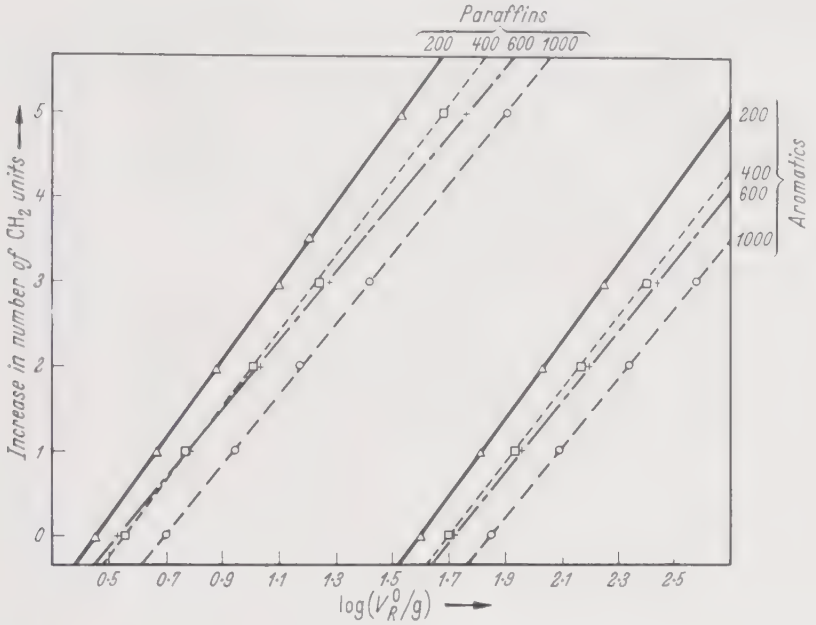

Figure 4. Relation between CH_2 *units and* log (V_R^0/g) *for paraffins and aromatics on PEG columns at* 100°C. *Numerals at ends of lines refer to molecular weight of stationary phase used*

Figure 4 shows a graph of log (V_R^0/g) against CH_2 units for paraffins and aromatics on the various PEG's. From this graph it can be seen that no useful increase in resolution has been effected with increasing molecular weight of the stationary phase, since the slopes of the lines alter very little. At the same time, the retention volumes of the paraffins have increased at a greater rate than those of the lower aromatics and so decane, which precedes benzene on PEG 200, nearly coincides on PEG 400 and 600 and emerges after benzene on PEG 1000. With the alcohols the retention volumes decrease with increasing molecular weight of the stationary phase (*Figure 5*) and so the effect is even more pronounced. *n*-Decane comes out well before methanol on PEG 200, a boiling point–elution inversion of 109C°, but comes out after ethanol on PEG 1000.

It is apparent that, by increasing the molecular weight of the PEG stationary liquid, one of its most useful properties is being lost and therefore the best liquid to use at a temperature of 100 C is PEG 200. If it is desired to operate at a higher temperature, PEG 400 must be used, although its ability to separate saturates from other compounds is smaller. No advantage is gained by using the higher molecular weight liquids since, as has already been seen, they are less stable thermally.

All the alcohols have much greater retention volumes than the other types of compounds with corresponding boiling points. This is presumably due to the formation of hydrogen bonds between the hydroxyl hydrogen of the alcohols and the ether links in the PEG and also between the hydrogen in the terminal hydroxyl groups of the PEG and the oxygen atoms of the alcohols. As the molecular weight of the PEG increases, the number of hydroxyl groups in a given weight of liquid decreases. Since the retention volumes of the alcohols decrease with increasing molecular weight of the stationary liquid, it is probable that the second type of bonding makes a significant contribution.

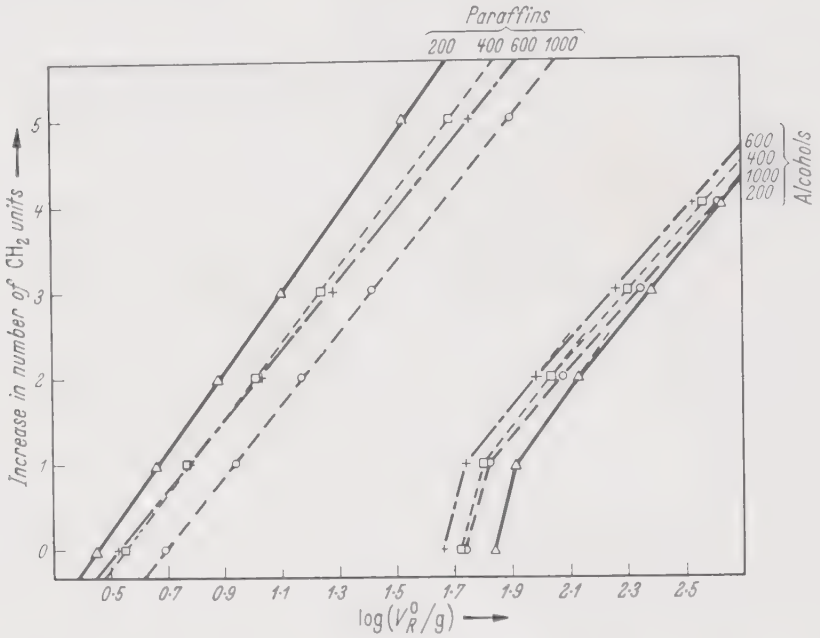

Figure 5. Relation between CH_2 *units and* $\log (V_R^0/g)$ *for paraffins and alcohols on PEG columns at* 100°C. *Numerals at ends of lines refer to molecular weight of stationary phase used*

Under similar conditions the retention volumes of the ketones increase and so here there can be no great contribution from the hydrogen bonds between the terminal hydroxyl groups of the polyglycols and the oxygen of the ketones. The same argument applies to the esters which behave in a similar manner. For the paraffins and aromatics, only van der Waals forces will act in the liquid phase, and since the paraffins are only held by dispersion forces, they pass through the column very quickly.

It will be recognized that the different types of compounds passing through the column are subjected to two counteracting effects:

(1) As the molecular weight of the polyglycols increases they become more lipophilic and the retention volumes of the less polar compounds increase.

(2) V_g values for all compounds will tend to decrease as the molecular weight of the polyglycols increases, since the molar concentration of the stationary liquid decreases. However, with the exception of the alcohols, the first effect predominates and the V_g values increase. If retention volumes per

Table II. Water Contents of Polyglycols

Substance	*Water content, %* w
PEG 200	0·70
PEG 400	0·55
PEG 600	0·22
PEG 1000	0·19
Methoxy PEG 350	0·30
PPG 425	0·29

Table III. V_g Values and Partition Coefficients for Compounds on PEG 400, Methoxy PEG 350, and PPG 425

Substance	*V^0/g at* 200 mm Hg *and* 100°C			*Partition coefficient at* 100°C (*Stationary phase*/N_2)		
	PEG 400	*Methoxy PEG 350*	*PPG 425*	*PEG 400*	*Methoxy PEG 350*	*PPG 425*
n-*Pentane*	3·56	5·73	9·24	2·98	5·58	8·95
n-*Hexane*	5·87	10·24	19·85	5·36	10·4	19·0
n-*Heptane*	10·23	18·47	40·60	9·85	19·1	38·6
n-*Octane*	17·38	34·07	80·22	17·1	35·6	76·0
n-*Decane*	48·71	110·6	—	49·3	117	—
Benzene	50·13	73·47	80·34	52·1	77·3	76·1
Toluene	85·94	132·6	159·4	89·7	140	151
m-*Xylene*	146·6	239·9	313·0	153	254	296
o-*Xylene*	188·9	303·2	382·4	198	321	362
Mesitylene	249·1	428·4	606·6	261	453	573
Methanol	52·62	55·50	49·81	54·6	58·3	47·2
Ethanol	62·89	70·99	65·28	65·5	73·7	61·8
n-*Propanol*	109·4	133·4	130·7	114	141	124
n-*Butanol*	199·4	256·7	270·7	209	271	256
n-*Pentanol*	362·3	495·3	554·2	380	524	524
Acetone	18·61	38·38	34·09	18·9	39·9	32·4
MEK	35·85	64·05	63·80	37·0	67·3	60·4
MIPK	44·19	80·32	89·33	45·8	83·6	84·6
DEK	59·42	102·6	113·8	61·8	108	108
MIBK	72·28	127·3	151·4	75·4	134	143
Ethyl acetate	38·39	53·30	60·37	39·7	55·9	57·1
n-*Propyl acetate*	63·54	94·28	115·9	66·2	99·3	110
n-*Butyl acetate*	108·6	173·8	227·7	113	184	215
Water	170·4	153·7	99·31	—	—	—

mole of stationary liquid had been compared, even the values for the alcohols may have shown a slight increase.

Methoxy PEG's 350, 550 and 750

The same compounds were run through columns containing these liquids as were run through the PEG columns. All the compounds had smaller retention volumes with increasing molecular weight of the liquid phase, although retention volumes on methoxy PEG 550 and methoxy PEG 750 were almost identical. The separations given by these liquids differed little from those

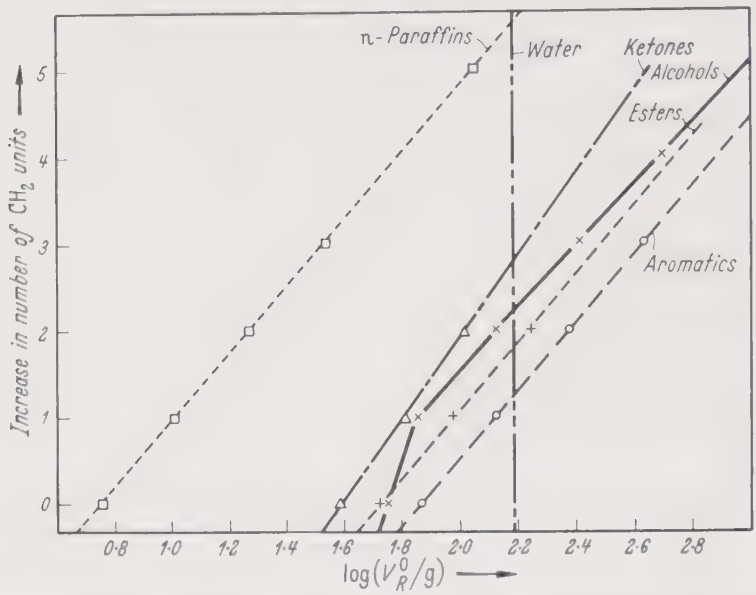

Figure 6. Relation between CH_2 *units and* $\log(V_R^0/g)$ *for various types of compounds on a methoxy PEG 350 column at* 100°C

Paraffins: n-pentane to n-decane. Aromatics: benzene, toluene, m-xylene, mesitylene. Alcohols: methanol to n-amyl alcohol. Ketones: acetone, methylethyl ketone, diethyl ketone. Esters: ethyl acetate to n-butyl acetate

given by the PEG's. The separation between paraffins and other types was poorer on the methoxy PEG's than on the parent glycols since the paraffins have a greater solubility in the former. There were small improvements in the separations of aromatic homologues and normal and *iso*-ketones, but the addition of a simple methyl group has only a small effect as far as GLPC is concerned. *Figure 6* presents a graphical illustration of the separating power of methoxy PEG 350. Decreasing thermal stability with increasing molecular weight was found in this group of liquids as in the PEG's (*Table 1*).

PPG's 425 and 1025

The solubility of the paraffins in these liquids was found to be so large that little type separation was obtained. The improvement in resolution of aromatics and ketones found in the methoxy PEG's was further improved on the PPG's (*Figure 7*; cf. *Figures 1* and *2*). It should be pointed out that, while the overall resolution of the ketones has improved, there is little alteration in the ratio of the partition coefficients of acetone to diethyl ketone. In spite of the fact that the PPG's gave a similar resolution of the homologous normal

ketones, they gave a better overall resolution because the ratio of the partition coefficients of adjacent normal and *iso*-ketones had increased.

Conversely, although the resolution of the series benzene—toluene—

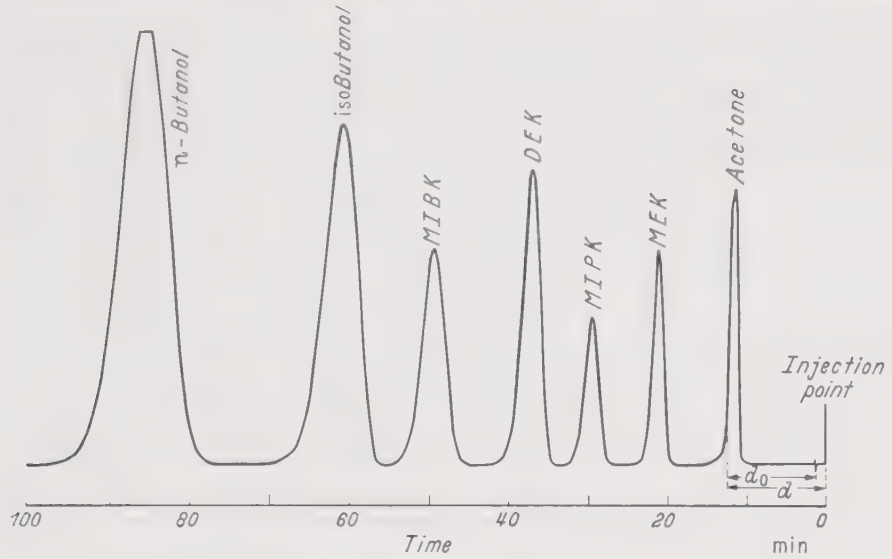

Figure 7. Ketones on a PPG 425 column at 100°C

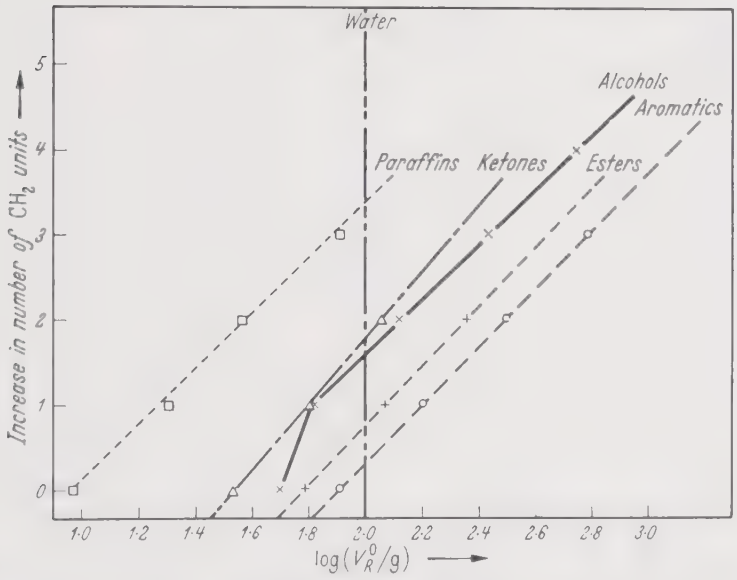

Figure 8. Relation between CH_2 *units and* $\log(V_R^0/g)$ *for various types of compounds on a PPG 425 column at* 100°C

Paraffins: n-*pentane to* n-*octane. Aromatics: benzene, toluene,* m-*xylene, mesitylene. Alcohols: methanol to* n-*amyl alcohol. Ketones: acetone, methylethyl ketone, diethyl ketone. Esters: ethyl acetate to* n-*butyl acetate*

m-xylene—mesitylene was better on PPG 425 than on PEG 400, the separation of *m*-xylene from *o*-xylene was better on the PEG 400. The resolution of aromatics on these liquids is good enough to warrant further investigation. *Figure 8* shows the separating power of PPG 425.

Analysis of mixtures containing water

The two main methods for the GLPC analysis of mixtures containing water have been published. The first method is to remove the water by some form of drying technique[7]. The second method is to use glycerol as the stationary

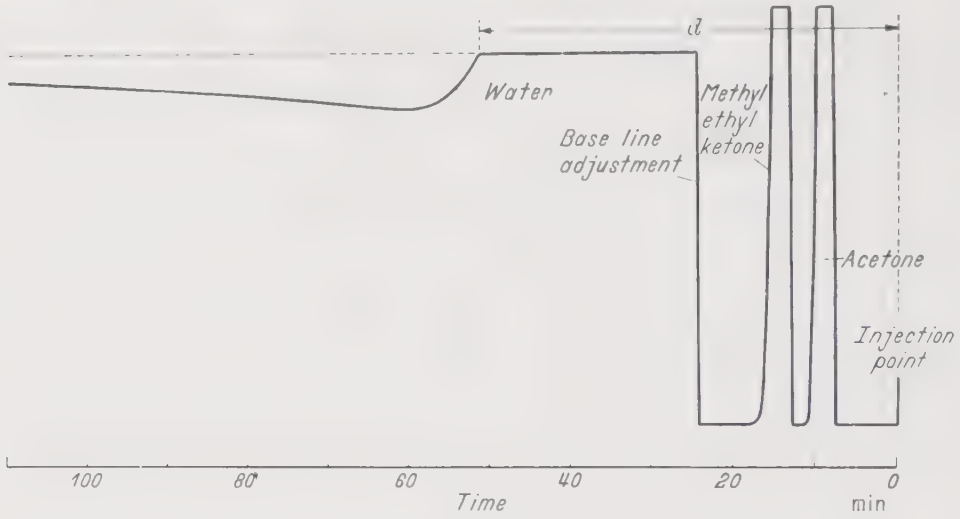

Figure 9. 6 mg *water on a PEG 600/Sterchamol column at* 100°C

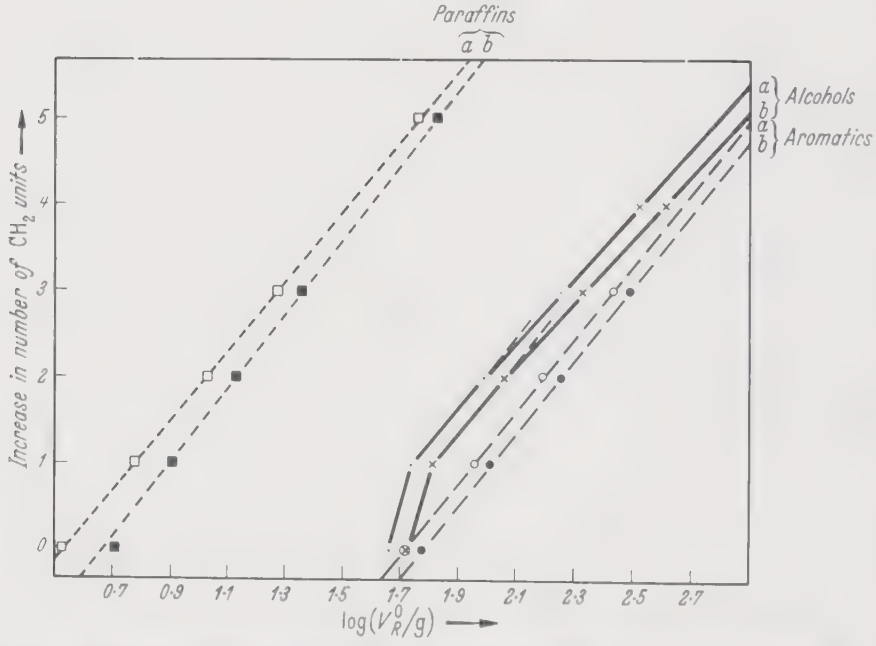

Figure 10. Relation between CH_2 *units and* $\log (V^0_R/g)$ *for various types of compounds on two different PEG 600 columns at* 100°C: (*a*) 28·6 per cent *PEG 600 on Sterchamol*; (*b*) 20 per cent *PEG 600 on Sterchamol*

liquid[8], since water has such a large retention volume on a glycerol column that most of the common organic solvents are eluted before the water. The second method of attack seems to be the more promising since most drying

techniques, unless they are rigorous and lengthy, leave enough water to interfere with the separation and determination of compounds on many stationary phases.

Aqueous mixtures were tried on all the liquids investigated, but in every case the result was a small negative peak with a long tail due to adsorption (*Figure 9*). The front of the water peak emerged late enough to permit the analysis of most common organic solvent mixtures, including all the lower ketones and the alcohols up to *n*-propanol, but the long recovery time needed by the column and the inability to obtain quantitative results for the water content limits the usefulness of the method.

The evidence for adsorption was strengthened by the fact that a column packed with a mixture of only 20 per cent PEG 600 on powdered brick gave consistently larger V_g values than those obtained on a column packed with a mixture containing the normal 28·6 per cent PEG 600 (*Figure 10*).

A column packed with 28·6 per cent PEG 600 on Celite 545, from which the fines had been removed by elutriation, gave water peaks which were good enough for quantitative work and still permitted the determination of the lower alcohols and ketones (*Figures 11* and *12*). Future work will disclose whether water contents can be accurately determined on such columns.

As the molecular weights of the PEG's are altered the retention times of the water peaks vary at a different rate from those of the various types of organic compounds examined. Since the polyglycol/Celite columns give good water peaks without excessive tailing the molecular weight of the stationary phase can be chosen to give the desired separation in any particular case.

Experimental and Results

The liquids used as stationary phases were all pretreated by heating to 100 C at a pressure of 1 mm of mercury for eight hours, to remove any volatile impurities and light ends. This resulted in weight losses of the order of 1–2 per cent. The vapour pressures were measured after heating to 100 C at 0·1 mm of mercury for 16 hours, a procedure found to be necessary in order to remove water present in the liquids which are all slightly hygroscopic (see *Table II* for water contents).

The support for the liquids was Sterchamol refractory brick, ground and sieved to 85–120 B.S. mesh (178–124 microns). The ground brick was heated to 160 C overnight and allowed to cool in a vacuum desiccator. The liquid was dissolved in a dry solvent, usually acetone, and the solution mixed with the requisite weight of brick powder (40 g of liquid to 100 g of brick). The mixture was heated with continuous stirring until all the solvent appeared to be removed; it was then heated to 100 C at a pressure of 1 mm of mercury for an hour, with occasional shaking during this period. Finally, the mixture was resieved to remove any fines made during the stirring and any larger particles caused by coagulation, especially when the substance was a solid at room temperature. The columns used were U-tubes of total length 184 cm, made from 6-mm internal diameter precision bore tubing to avoid the gross variations in volume which result when ordinary tubing is used. The majority of the columns had a volume of 52·5 ml; a few varied from this by not more than ± 0·5 ml. Each column was packed by resting the bottom on a small plastic anvil attached to a Pifco Vibratory Massager and

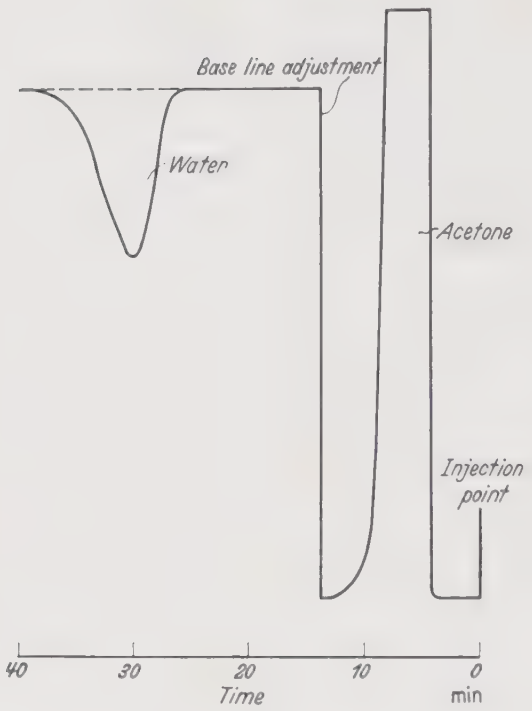

Figure 11. 1 mg *water on a PEG 600/Celite 545 column at* 100°C

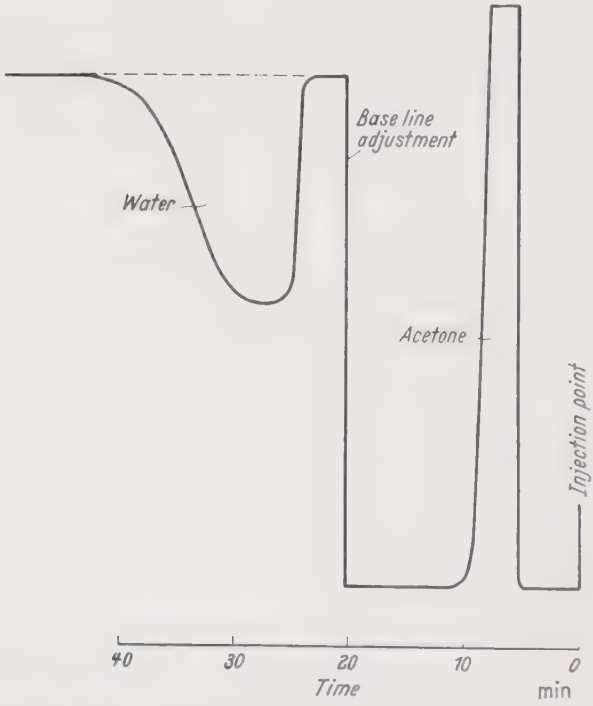

Figure 12. 8 mg *water on a PEG 600/Celite 545 column at* 100 C ($\frac{1}{4}$ *sensitivity*)

adding the brick powder holding the liquid phase, until a packing density of about 0·6 g/ml was obtained.

In the apparatus, the column temperature was maintained constant at 100 C by means of a vapour jacket. Oxygen-free nitrogen was used as the carrier gas exclusively, with flow rates of about 1 l./h at s.t.p.: the flow rate

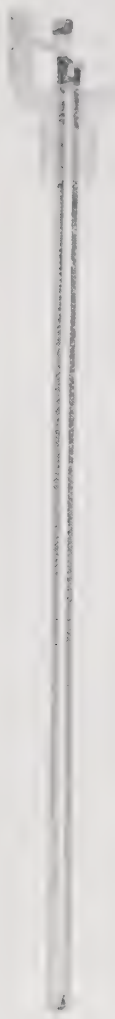

Figure 13. Type of column used for study of stationary liquids

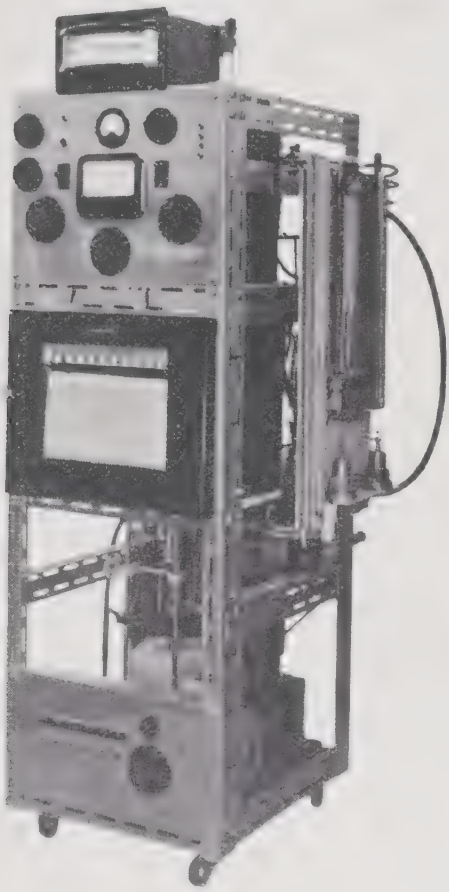

Figure 14. View of apparatus showing gas controls

was measured with a capillary flowmeter on the inlet side of the column. The inlet and outlet pressures were controlled by Negretti & Zambra valves, Type No. R/182. The outlet pressure was kept constant at 200 mm of mercury and the inlet pressure set to give the required flow rate. All the columns were given at least eight hours to settle down before the various samples were run. The sample size was 25 µl (about 20 mg) but since the various homologous series were made up in a suitable solvent which did not

interfere with the chromatogram, the maximum amount of any one substance was 5 mg. The detector in all cases was a two-cell katharometer with both cells on the outlet side of the column and a liquid air trap between them. *Figures 13*, *14* and *15* show the columns and apparatus used.

Throughout this work, the retention distance (d) of a peak on the recorder chart was measured from the injection point to the intercept of the tangent to the rear of the peak with the base line (see *Figure 7*). The distance to the

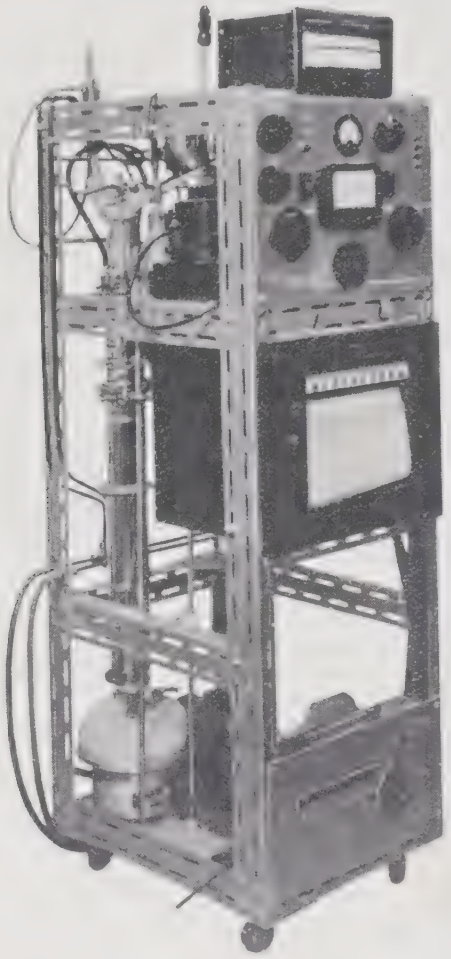

Figure 15. View of apparatus showing column in position

rear of the peak appears to be more reproducible, and less dependent on sample size, than the distance to the front or centre. Two exceptions were made to this mode of measurement. For water, the retention distance was measured to the tangent to the front of the peak since tailing rendered the former method impossible (*Figure 9*). For calculating the column efficiency (*Figures 1* and *2*), the retention distance was measured to the centre of the peak. For the calculation of the limiting retention volume (V_R^0) the usual

corrections for dead-space, pressure drop and temperature were made. Since the flow rate of the nitrogen was measured on the inlet side of the column a further correction was necessary to obtain the flow rate at the outlet pressure.

Example:

Column PEG 200 Chart speed = 12 in/h = 30·48 cm/h
Temperature 100°C
Flow rate 1030 ml/h of nitrogen at 640 mm of mercury and 20°C
Inlet pressure 640 mm of mercury
Outlet pressure 200 mm of mercury
Dead-space (i.e. distance to air peak) 0·48 cm
Distance to rear of *m*-xylene peak 16·48 cm
∴ True retention distance = 16·48 cm − 0·48 cm = 16·00 cm

$$V_R = \frac{16{\cdot}00}{30{\cdot}48} \times 1030 \times \frac{640}{200} \times \frac{373}{293} = 2202 \text{ ml of nitrogen at 200 mm of mercury and 100°C}$$

$$V_R^0 = V_R \cdot \frac{3}{2}\left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}\right]$$

$$= 2202 \cdot \frac{3}{2}\left[\frac{(640/200)^2 - 1}{(640/200)^3 - 1}\right] = 960{\cdot}8 \text{ ml of nitrogen at 200 mm of mercury and 100°C}$$

The partition coefficients were calculated from a formula derived from one given by James and Martin[1].

$$\alpha = \frac{A_L/A_S}{\frac{A_L l}{V_R} \cdot \frac{2}{3}\left[\frac{(p_i/p_o)^3 - 1}{(p_i/p_o)^2 - 1}\right]} - \frac{A_L}{A_S}$$

where A_L = cross sectional area of the gas phase, A_S = cross sectional area of the liquid phase, V_R = retention volume at the temperature and outlet pressure of the column, p_i = inlet pressure of column, p_o = outlet pressure of column, and l = length of column.

The values of V_g and α for the best columns in each of the three series are given in *Table III*.

The author wishes to thank the Directors of 'Shell' Research Limited for permission to publish these results, Dr A. D. Shellard and Mr D. W. Morecroft who did the vapour pressure measurements, Mr S. A. Bingham, and all those at Thornton who helped in this work.

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DISCUSSION

A. G. Davison: PEG 200 has been used as liquid phase for the separation of complex mixtures of unknown substances of biological origin. These substances occur at low concentration in an aqueous medium and are for various reasons not susceptible to extraction by organic solvents. Material is applied in aqueous solution, the water content being sometimes as high as 99·9 per cent, and the various components are well separated from water with no adverse effects on the column. This is even so when the column is grossly overloaded with respect to water. Separations have been carried out at temperatures of 56 and 100°C.

When eluted substances have been condensed after separation on columns containing PEG 200 at 100°C there has been evidence of stationary phase in the cold trap. The 400 molecular weight polymer may be more suitable for this type of work.

A. Klinkenberg: I would like to comment about the maximum vapour pressure in stationary liquids. Is it possible to make a statement in simple terms such as, that during the useful life of the column one is not allowed to evaporate more than, say, 20 per cent of the stationary liquid originally present? I tried to calculate values from Mr Adlard's paper but I did not succeed because I did not know how much stationary liquid was present originally in the column which was mentioned. However, if I did it correctly, I worked out that during the useful life about 4 g of the 400 molecular weight polyglycol had evaporated. If we knew how much was present originally we might make a guess at the ratio.

E. R. Adlard: The only answer I can make to Dr Klinkenberg's comment is to tell him how much was present in the first place. I cannot do that offhand but I can later on if that will satisfy him.

E. Glueckauf: I would have thought that the answer to this problem is that if one is seriously concerned with the evaporation of the stationary phase then one ought to pre-saturate one's gas stream at the appropriate temperature to the stationary phase, and then no evaporation would take place and the column would last so much longer.

M. M. Wirth: It is usual to choose a stationary phase with a very low vapour pressure at the temperature of analysis. This is desirable for routine analysis when the column must be used many times. It is, however, by no means essential and in research work there is no reason why one should not use a relatively low-boiling stationary phase provided it is somewhat higher-boiling than the sample to be analysed. Thus we have analysed C_5-hydrocarbons (b.pt. 30–50°C) using acetone as a stationary phase at 0°C. The column cannot be used again unless the carrier gas is pre-saturated with stationary phase.

C. M. Drew: I would like to comment on the evaporation of the stationary phase. Some workers are packing the exit end of the column with about two feet of a dry inert support and having the front of the column packed with wet support. This means the stationary phase will migrate into the dry material for some period of time before it begins to appear from the exit of the column. This serves as a very nice way of increasing the effective life of the column. However, it does require that the support material be rather inert.

F. van der Craats: Concerning the evaporation of the liquid phase, we also used more or less volatile liquid phases, and by pre-saturation of the carrier gas it was not possible to keep the column in good condition, especially when the columns were long and there was a pressure drop over them. Your carrier gas is saturated with the liquid at the pressure at the entrance of the column, but as long as the pressure falls to the end of the column there is always new evaporation. Also, I think the idea of having a portion of dry carrier material after your main column, so that your liquid phase will travel gradually through, does not hold. When it is evaporated at a certain point, there is no reason for condensation again.

10

A PRELIMINARY STUDY OF SOME FACTORS INFLUENCING THE ORDER OF ELUTION OF HALOGENATED METHANES, THE DEGREE OF SEPARATION, AND THE REPRODUCIBILITY OF RETENTION VOLUMES IN GAS–LIQUID PARTITION CHROMATOGRAPHY

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University of Bristol

The order of elution of a series of halogenated methanes has been shown to depend upon the nature of the liquid phase, and in the case of water as a liquid phase, upon the amount present. These compounds are eluted in order of boiling point upon columns containing liquid paraffin, and silicone fluid 702, but partial or complete inversion of this order is obtained on columns containing dibutyl phthalate, dinonyl phthalate, glycerol, and water. Evidence is presented for specific interaction of certain liquid phases with halogenated-methanes containing one hydrogen atom. Approximate partition coefficients from static experiments are in agreement with coefficients calculated from corrected retention volumes per gramme of static liquid phase.

The effect of temperature and flow rate upon retention volumes and separation efficiency for these compounds is considered. The efficiency of a column is confirmed as being dependent upon the type of solute, the retention volume, and the type of liquid phase. The influence of time of injection of gases, and time of injection and temperature of injection of liquids, upon the separation efficiency is briefly described. A comparison is made of the separation efficiency of a static liquid phase supported on (*i*) glass powder, and (*ii*) on kieselguhr. Different methods of dispersion of the liquid on the kieselguhr are considered. The asymmetry of eluted peaks is shown to depend upon the type and amount of the solute. As the amount increases, an ethanol peak changes from having a sharp front to having a sharp rear, whereas chloro-methanes change from symmetrical peaks to peaks having sharp fronts.

The factors which affect the separation of substances by vapour phase chromatography have already been investigated and discussed by a number of workers (James and Martin[1]; Keulemans *et al.*[2]; Littlewood *et al.*[3]; Purnell and Spencer[4]).

The purpose of this communication is to report our independent investigations on the behaviour, particularly, of halogenated hydrocarbons on partition columns with liquid phases of different types, and the conditions under which the columns are operated.

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Experimental

Apparatus and procedure

The apparatus and procedure were essentially similar to those of previous workers, e.g. Ray[5], and arranged with an alternative gas–liquid partition column of 180 cm total length and 4 mm internal diameter, or a charcoal column of 30 cm length and 4 mm internal diameter. (The inlet of the column had a heated and lagged injection port, the temperature of which could be varied.) The thermal conductivity cell was all glass with platinum wire filaments and surrounded by a glass vapour jacket.

The packings of the chromatograph columns were either Celite 545 sieved to 100–200 B.S.S. mesh after sedimentation and drying for three hours at 120 °C, or Sutcliffe, Speakman grade 208B charcoal ground and sieved to 60–80 B.S.S. mesh and dried by passing nitrogen through the packed column at 137°C.

With the partition columns, the exact amount of liquid phase present in the packed column was determined as follows:

(*i*) for relatively involatile liquids, a known weight of Celite was mixed with a known amount of the liquid phase dissolved in acetone, the latter removed by evaporation in an electric oven, and the 'dry' mixture reweighed to find the amount of liquid phase held by the Celite. A weighed portion of this was then used to pack the column.

(*ii*) for water (or similarly volatile liquids), the Celite was mixed with the required amount of distilled water, and weighed before packing the column. After a series of runs, the column material was weighed again to find the amount of water which had been lost to the nitrogen stream during the experiments. The mean quantity of water held on the Celite during the runs was thus found. This procedure is necessary for any volatile liquid likely to be stripped from a column packing during the passage of the gas stream.

The experimental retention volumes were corrected for dead-volume, flowmeter temperature and atmospheric pressure, pressure ratio across the column, and weight of liquid phase, as described by Littlewood *et al.*[3].

Results

Variation of the order of elution of halogenated methanes with type of liquid phase—The retention volumes for a series of (*a*) chloro-methanes, and (*b*) fluoro-chloro-methanes, on partition columns with different types of stationary liquid phases are given in *Tables I* and *II* respectively. For comparison purposes, the retention volumes on a charcoal column of some of these halogenated methanes are included in *Table II*.

On non-polar or low polarity liquid phases, i.e. liquid paraffin, silicone 702, and silicone 1107, the halogenated methanes are eluted in the order of their boiling points and molecular weights.

With the more polar liquid phases, i.e. dinonyl phthalate and dibutyl phthalate, a similar order is observed except for those compounds with one H atom substituted, i.e. $CHCl_3$, CF_3H, CF_2ClH, and $CFCl_2H$. With each of these, the retention volumes are greater than would be anticipated from their boiling points and molecular weights. The effect is most marked with $CHCl_3$ which is held back on the column and eluted after CCl_4.

For a more strongly polar liquid such as glycerol, the retention volume for CCl_2H_2 is also increased causing this compound to be eluted after CCl_4. The behaviour on partition columns with water as the stationary phase will be discussed in more detail later in this paper.

Table I

Liquid phase	*Weight* g	*Temp.* °C	*Corrected retention volume* per gramme V_g			
			CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Kieselguhr	3·00	27·3	—	1·5/3g	2·25/3g	2·34/3g
Dibutyl phthalate	4·0	57·0	—	108	254	182
Dinonyl phthalate	1·89	57·2	27·3(24·5)	82·8	210	173
Silicone 702	2·14	56·7	10·0	60·5	136	180
Silicone 702	2·14	20·2	25·1	232	595	746
Silicone 1107	1·98	19·5	—	149	390	565
Glycerol	2·27	24·4	2·16	12·9	16·75	3·85
Liquid paraffin	1·85	56·6	—	33·8	87·6	170
Water	1·72	24·2	—	14·7	5·95	1·70

To obtain approximate 'bulk phase' partition coefficients of the group CH_2Cl_2, $CHCl_3$, and CCl_4, a study was made of the partition of the vapour of each chloro-methane between the gas phase and a liquid phase of silicone 702 and dinonyl phthalate respectively. A simple tensiometric method was used

Table II

	Column	4·0 g *Dibutyl phthalate*	1·89 g *Dinonyl phthalate*	2·14 g *Silicone 702*	1·83 g *Charcoal 207B*
Boiling point	*Temperature*	20°C	24·5°C	40·1°C	137°C
	Compound	*Corrected retention volume* per gramme V_g			
−82·2	CF_3H	2·5	1·8	0·45	7·6
−80	CF_3Cl	0·6	0·6	0·54	17·3
−40·8	CF_2ClH	21·6	17·3	5·57	53·0
−28	CF_2Cl_2	8·3	9·5	6·10	152
8·9	$CFCl_2H$	88·0	131·5	41·0	453
24·1	$CFCl_3$	171	80·5	47·0	1160
−23·7	CH_3Cl	—	27·3	22·0	57·5

to determine the amount of chloro-methane vapour in the gas phase which was in equilibrium after a period of contact, 30–60 minutes with a known weight of liquid silicone 702 or dinonyl phthalate contained in a closed vessel. From the weight of chloro-methane which was admitted to the vessel initially, and the quantity which remained in the vapour phase, it was possible to calculate the amount which had gone into solution under these conditions

in either silicone 702 or dinonyl phthalate. The partition coefficient (α) was calculated as the weight of vapour per unit volume of liquid phase/weight of vapour per unit volume of gas phase. Though no great accuracy is claimed for the method used, it will be seen from *Figure 1* that the values of α for each of the chloro-methanes with silicone 702 are very different, and increase with boiling point. With dinonyl phthalate the values for $CHCl_3$ become similar to those for CCl_4 and are in agreement with the order of elution.

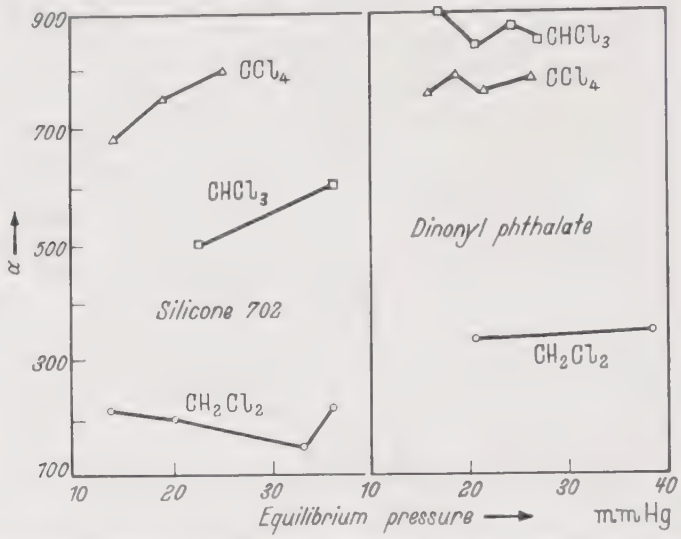

Figure 1. Comparison of partition of chloro-methanes with silicone 702 and dinonyl phthalate

From the V_g values for the above compounds eluted from columns of silicone 702 and dinonyl phthalate, the effective partition coefficients can be calculated from the relationship[3] $V_g = 273\rho\alpha/T$, where ρ is the density of the static phase, and T the column temperature in K. The mean values for α from *Figure 1* are compared in *Table III* with the values for α calculated from the V_g values. For silicone 702 the V_g values were determined experimentally at

Table III

		CH_2Cl_2	$CHCl_3$	CCl_4
Silicone fluid 702	*Mean static* α	204	562	735
	V_g *calc.* α	232	595	746
Dinonyl phthalate	*Mean static* α	338	878	770
	V_g *calc.* α	377	1010	743

20°C, but those for $CHCl_3$ and CCl_4 on dinonyl phthalate were obtained by extrapolation from a plot of log V_g against $1/T$. The V_g value for CH_2Cl_2 on dinonyl phthalate was determined on a large column containing 14·6 g of liquid.

It will be seen that there is agreement in the values of α obtained by the two independent methods.

The variation of order of elution of chloro-methanes with the amount of liquid phase—(a) *Water partition columns.* The retention volumes were determined for the series CH_2Cl_2, $CHCl_3$, CCl_4 on columns of kieselguhr, both dry and

also with varying quantities of water as the stationary phase. During the elution process, water from the column was lost to the gas stream at a constant rate of 0·23 % w/w/100 ml of nitrogen. As stated earlier in this paper, the quantity of water present at the time of each elution was corrected for this

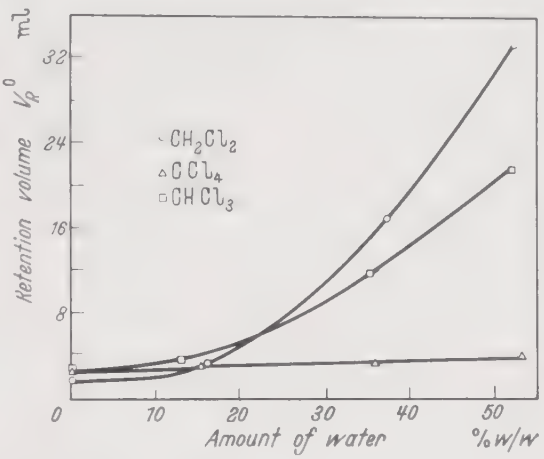

Figure 2. Corrected retention volumes of chloro-methanes as functions of water content of column

loss. *Figure 2* shows the plot of the corrected retention volumes (V_g^0 vs wt of water) against the percentage (w/w) of water on the column. At about 50 % w/w water, the kieselguhr became saturated so that retention volumes with higher percentages of water could not be determined. Retention volumes for the chloro-methanes on specially dried kieselguhr (i.e. 24 hours drying instead of 3 hours) were slightly higher than the values for dry kieselguhr given in *Figure 2*.

The interesting features of these experiments were the variations in order of elution which occurred with increasing water content. These are summarized thus:

Dry kieselguhr . .	CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4
With 0–15 % water .	CH_2Cl_2, CCl_4, $CHCl_3$
With 15–25 % water .	CCl_4, CH_2Cl_2, $CHCl_3$
With 25–50 % water .	CCl_4, CH_3Cl, $CHCl_3$, CH_2Cl_2.

It will be observed that on kieselguhr alone, the order of elution is that of the order of the vapour pressures of the chloro-methanes. With water, the order gradually changes until it is in the order of the solubilities of the chloro-methanes in water.

(b) *Dinonyl phthalate partition columns.* The retention volumes of the three chloro-methanes on kieselguhr containing varying amounts of dinonyl phthalate at 57 °C are given in *Table IV*. The columns were operated at approximately the same pressure ratio and the values of V_g agree to about 5 per cent.

The order of elution, CH_2Cl_2, CCl_4, $CHCl_3$ does not alter with the amount of liquid phase and is that of the vapour pressures.

Further experiments will be carried out to test the effects with glycerol (which we anticipate may behave like water), and dibutyl phthalate, as well as other liquid phases.

Effect of column temperature on the V_g value—The variation of the V_g value for a series of halogenated hydrocarbons on silicone 702, dinonyl phthalate and glycerol partition columns respectively has been investigated in detail, and will be presented in a future paper. For all examples investigated, the variation of log V_g with $1/T$ has been found to be linear, and this is in general agreement with the work of Littlewood *et al.*[3], who have made similar studies with alcohols, esters, and aromatic hydrocarbons on partition columns of silicone 702 and tritolyl phosphate.

Table IV

Amount of dinonyl phthalate	*Pressure ratio*	V_g CH_2Cl_2	V_g CCl_4	V_g $CHCl_3$
0·92 g	1·17	88	185	216
1·89 g	1·18	83	174	210
14·6 g	1·14	87	—	—

Effect of variation of flow rate on the V_g value and efficiency of separation—The V_g values obtained for chloro-methanes on dinonyl phthalate columns operated at different pressure ratios, and therefore different flow rates, were found to fluctuate from day to day by about ± 5 per cent. This made it difficult to make an exhaustive study, but a series where care was taken to keep all factors (apart from flow rate) constant was performed with $CHCl_3$ on a 1·85 g liquid paraffin column at 57°C (*Table V*).

Table V

p_1/p_0	1·260	1·215	1·182	1·149	1·138
Flow rate ml/min	70·3	56·8	47·8	37·9	35·2
V_g	162	163	163	162	164
Plate number	182	208	234	258	254

The agreement is very good, the maximum deviation from the mean being only 0·6 per cent. These results were obtained with the assistance of Mr T. B. Gay. The plate number was calculated from the formula given by Littlewood *et al.*[3] and shows the increase in efficiency with decrease in flow rate.

The influence of the solid phase and the dispersion of the liquid phase on the V_g value and the efficiency—The nature of the solid support and its influence on the elution of chloro-methanes was investigated on (*a*) powdered glass as a non-porous solid, and (*b*) on kieselguhr.

The use of a porous solid support appears to be necessary since a column prepared by adding 0·8 g of dinonyl phthalate to 10 g of Hysil grade 1 glass powder gave no separation whatsoever with the chloro-methanes. Experiments with a sample of petrol ether (b. pt 40–60°C) on (*i*) a glass powder column at 15 C immediately gave one sharp peak, and on (*ii*) a dinonyl

phthalate–glass powder column there was a long low peak which had a V_g value of 60 ml at its maximum. The approximate plate number for a 3 μl peak of *n*-pentane was 3 for the same dinonyl phthalate–glass powder column, compared with 390 for a dinonyl phthalate–kieselguhr column (0·9 g DNP/3 g kieselguhr).

The two samples of column material of dinonyl phthalate–kieselguhr were prepared by different methods. For sample I, the liquid phase was dispersed on the kieselguhr by continued stirring, while for sample II the liquid phase was first dissolved in acetone, then well stirred with the kieselguhr, and the acetone subsequently removed by evaporation. These materials were used to prepare two similar columns, I and II respectively.

The V_g values for three chloro-methanes determined on each of the two columns were found to agree within 2 per cent, but the effective plate number of column II was greater than that for column I. For example, the plate number of a 1 μl peak of CH_2Cl_2 was 260 for column I, and 530 for column II. It is apparent that a column may be more efficient where the liquid phase is more evenly and thoroughly dispersed over the solid support.

Variation of the efficiency of separation with the type of compound and the retention volume—Elution of equal volumes of CH_2Cl_2, $CHCl_3$, and CCl_4 under similar conditions on a column of 2 g of dinonyl phthalate at 40°C showed that the efficiency of the column increased with increase in retention volume, e.g.

	CH_2Cl_2	CCl_4	$CHCl_3$
V_g	108	246	347
Plate number	450	535	650

A similar effect has been found with the elution of compounds in a homologous series, e.g.

	Methyl-ethyl ketone	Methyl-*n*-propyl ketone	Methyl-*iso*butyl ketone	Methyl-*n*-amyl ketone
V_g	32·5	65·3	91·6	228
Plate number	326	355	588	830

The values for ketones were determined on 2 μl samples injected into a column containing 2 g of silicone 702 at 97°C.

Littlewood *et al.*[3] have also reported that different types of compounds having similar retention volumes on a given column, frequently have different effective plate numbers. The following values demonstrate this effect: methyl-*n*-amyl ketone 830 plates, bromoform 272 plates on the silicone 702 column under similar conditions; also acetic acid 127 plates, methyl-ethyl ketone 326 plates.

Variation of efficiency and V_g value with amount of sample—A preliminary study was made of the injection of amounts of ethanol from 5 μl to 20 μl into a column containing 2 g of dibutyl phthalate at 57 C. As the amount was increased, the peaks became markedly asymmetrical with sharp rears and tailing fronts. The retention volume to the peak maximum increased linearly with increase of the amount injected. The plate number for the column decreased from 400 for 5 μl samples to 100 for 20 μl samples.

The variation of V_g, and separation efficiency, with amount injected was studied in greater detail for chloro-methanes on a column of dinonyl phthalate at 40 °C. A constant volume of 10 μl of liquid was injected consisting of 5 μl of acetone and 5 μl of a mixture of CH_2Cl_2, $CHCl_3$ and CCl_4, in various proportions. The time to the maximum of each peak was measured, and *Figure 3* shows the family of peaks for amounts of $CHCl_3$ from 0·5–5 μl (i.e. 10 % v/v to 100 % v/v in mixtures with CH_2Cl_2 and CCl_4). Similar families of peaks have been obtained with CH_2Cl_2 and CCl_4. As the amount

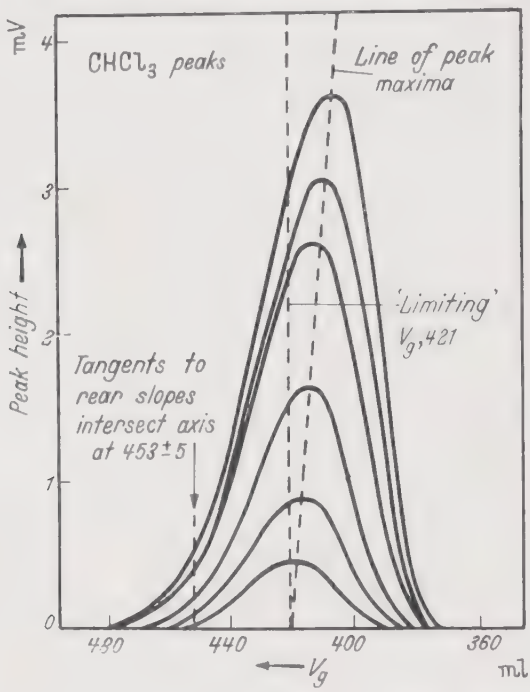

Figure 3. Showing line of peak maxima for various amounts of $CHCl_3$

increased, the retention volume of the maximum decreased, and *Figure 4* shows a plot of the amount injected against *R*, the retention volume of maximum of $CHCl_3$ peak/retention volume of maximum of acetone peak (the absolute retention volume is also indicated). The retention volume of the 5 μl acetone peak in all the above work was constant to ±2 per cent.

There was a considerable increase in efficiency with decrease in amount injected (*Figure 5*).

With the above-mentioned families of peak curves, the rear slopes are reasonably reproducible and a tangent to the rear slope for each peak cuts the base line at a point which is reproducible to ±1 per cent. Littlewood *et al.*[3] have reported a similar effect for peaks of alcohols, esters, and aromatic hydrocarbons, but with these compounds the peaks are asymmetrical in the opposite direction, and the front slope is reproducible. They have proposed an empirical procedure for correction of the retention time of such peaks. The time between the peak maximum and the end of the peak is added to the time to the beginning of the peak. It is often difficult to apply in practice, however, unless very sharp peaks are obtained. This empirical method has not been found to hold for the above peaks of chloro-methanes. The line through the

points of maximum concentration for the family of peaks cuts the base line at the retention volume at which an infinitesimally small amount of vapour would be eluted under the given conditions. This volume could therefore be taken as the characteristic retention volume for the given vapour on the given column.

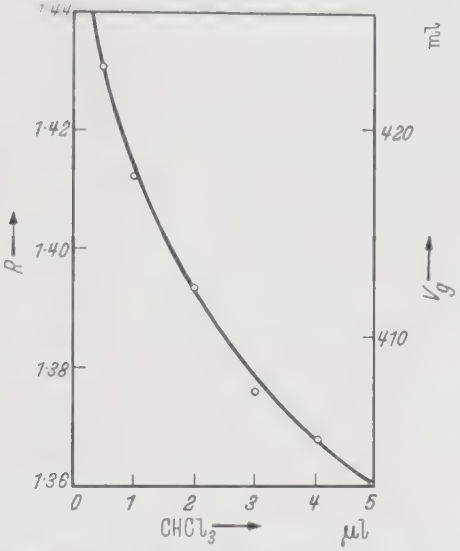

Figure 4. Amount of $CHCl_3$ *injected as a function of R (see text)*

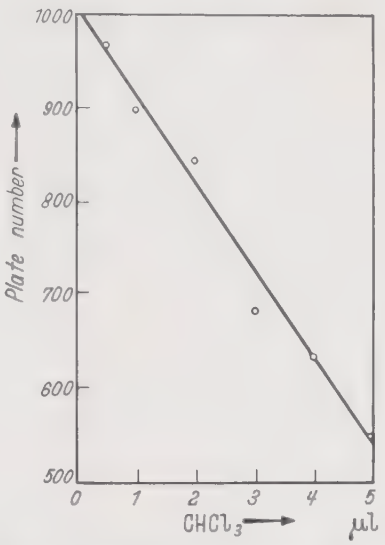

Figure 5. Relationship between efficiency and amount of $CHCl_3$ *injected*

Effect of variation of time, and temperature, of injection upon the efficiency of separation—To determine whether more rapid injection of liquid samples from a micrometer syringe would lead to higher efficiency of separation, 10 μl samples of *n*-pentane were injected over time intervals of 3–20 seconds at constant flow rate and injection temperature. The peak height and efficiency of separation were constant to ± 1 per cent for times up to about 10 seconds, but above this time there was a significant decrease in efficiency.

The effect of temperature of injection has been described previously[6], and the efficiency shown to depend upon the temperature at low temperatures (< 40° C for chloro-methanes) with the injection port and technique described. Above this temperature the efficiency became independent of temperature for chloro-methanes, but some increase in efficiency was found for alcohols.

Review

Since the experimental work described in this paper was completed, Keulemans *et al.*[2] have discussed in general terms the part which the stationary phase in a partition column can play in vapour phase chromatography, and have illustrated their work with examples of hydrocarbons of different types. Our investigations with halogenated hydrocarbons confirm still further that the choice of the stationary liquid is an important factor, and also that the amount of liquid phase may be important with certain liquid phases, e.g. with water.

The halogenated methanes are eluted in the order of boiling point and molecular weight with liquid phases of liquid paraffin, or silicone 702, or

silicone 1107. These stationary phases are essentially non-polar liquids, and the attractive interaction between solute and solvent is of the London type exclusively.

On dinonyl phthalate and dibutyl phthalate liquid phases, chloroform is held back relative to carbon tetrachloride, and fluoro-chloro-methanes with one unsubstituted hydrogen atom also have slightly higher V_n values than the corresponding compounds with chlorine substituted for hydrogen. This indicates a specific interaction of the liquid phase with the halogenated methanes containing one H atom.

The bulk phase partition coefficients determined for chloroform and carbon tetrachloride are in agreement with those calculated from the experimental values of V_g. This was also found by Bradford *et al.*[7] for hydrocarbons on a column of tri*iso*butylene.

With a partition column of glycerol, carbon tetrachloride is eluted before chloroform or methylene dichloride. This observation suggests that with such a highly polar solvent, a non-polar molecule like carbon tetrachloride has a low partition coefficient and hence a low V_n. The order of elution of the polar members of the series is determined by the extent to which they interact with the glycerol phase. James *et al.*[8] have shown that the elution of amines on a glycerol column depends upon the structure of the amines.

The order of elution of the chloro-methanes on kieselguhr alone is in the order of vapour pressure, whereas with relatively large amounts of water on the kieselguhr, the order is that of solubility. With smaller amounts of water present, the order of elution depends upon the relative contributions of the two effects—adsorption on the solid, and solution in the liquid phase. In such cases the solid support may considerably influence the separation of substances.

Purnell and Spencer[4] have also studied the behaviour of a series of chloro-methanes on 'dry' kieselguhr, 'wet' kieselguhr, and kieselguhr wetted with water containing Teepol. The retention volumes show that the order of elution is that of increasing chlorine content of the chloro-methanes, the values of the retention volumes are less when water is present on the kieselguhr, but increase somewhat when Teepol is added to the water. It is difficult to reconcile the observations which we have made about the change in the order of elution when the water content is increased with those of Purnell and Spencer. The latter workers may have failed to correct for the loss of water to the gas stream which we find to be important even when the experiments are carried out rapidly. The percentages of water at which the order of elution changes (*Figure 2*) appear to depend upon the source and method of preparation of the kieselguhr. Further work on more thoroughly dried kieselguhr as starting material may give more reproducible results between different workers.

Since a constant V_n value is of great importance for identification of substances as proposed by Littlewood *et al.*[3], it is necessary to establish that the V_n values for any liquid phase are independent of the amount of liquid phase on the column. Our work indicates that this factor is important with a liquid like water, but not for dinonyl phthalate, and further work is planned to study other highly polar liquids such as glycerol.

The variation of V_n value with column temperature has only been mentioned

briefly in this paper since plots of V_g against column temperature for a number of halogenated hydrocarbons are in course of publication. The plots will allow the qualitative analysis of these compounds to be carried out based on their V_g values on one or more column liquids.

The correction of measured retention volumes to V_g values on columns operated at varying pressure ratios and flow rates has shown that the V_g value is independent of flow rate over the range studied and that the plate number for a column increases with decreasing flow rate. This is in agreement with the work of James and Martin on the correction of retention volumes, and these authors further show that a limit to the increase of plate number is reached at relatively low flow rates when lengthwise diffusion along the column becomes important.

James and Martin[8] found that in elutions from kieselguhr containing a liquid phase the kieselguhr was not inert, but adsorbed the vapours of amines and fatty acids and produced tails to each peak. Elution from a column containing no liquid phase gave badly tailing peaks and this has been confirmed for halogenated methanes in the present work. The influence of the kieselguhr upon the retention volume and order of elution is well shown with water as the liquid phase. However, Bradford *et al.*[7] conclude from work on tri*iso*butylene columns that solution in the thin layer of liquid (10^{-3} mm thick) occurs with no appreciable interaction with the support. The agreement of α determined by two different methods for chloro-methanes on silicone 702 and dinonyl phthalate (*Table III*) supports this. Further study of this series, and other solutes, on water and other liquid phases may yield results of fundamental importance.

From the limited work described, a porous support appears to be necessary for high efficiency. Normal glass powder with an added liquid phase gave inefficient columns and was not convenient to pack, but porous glass can be prepared and may function as a suitable column material having a comparatively easily controlled pore-size distribution. A study of the effect of pore size on efficiency could be conveniently carried out on such a material. Preliminary experiments have indicated that different methods of dispersion of the liquid phase upon the support give columns of different efficiencies and further work is planned to study methods of increasing the column efficiency.

The effect of the type of compound and the V_g value on the efficiency of a given column confirms the work of Littlewood *et al.*[3]. Sufficient work has not been carried out to place these effects upon a strictly quantitative basis, and the results of other workers are difficult to compare since the efficiency can depend markedly upon experimental technique and possibly upon the characteristics of the recording equipment.

The amount of sample passed through the column has a considerable effect upon the V_g value and the efficiency of the column. It is therefore an advantage to carry out qualitative and quantitative analysis with the lowest amounts which can be detected satisfactorily, and where possible to use less than 1 μl of liquids. Increase of the sensitivity will therefore be of considerable interest, both from the possibility of analysing even smaller amounts, and from the simplification of the correction of retention volumes. When amounts of less than 1 μl are analysed on the size of column described above,

the peaks tend to be approximately symmetrical and correction for asymmetry is less than 1 per cent. Of interest in this work is the dependence of direction of asymmetry of peaks on the type of compound. On our apparatus, sharp front-slopes have been obtained for chloro-methane peaks, with the retention volume to the maximum decreasing with increase of amount eluted, whereas the opposite applies for alcohols (see also Littlewood *et al.*[3] for shape of peaks of alcohols and esters). This effect depends primarily upon the direction of curvature of the partition isotherm, and the determination of isotherms on a number of liquid phases would be of value to confirm this. Asymmetrical peaks could also be due to different rates of reaching equilibrium from the gas phase and from the liquid phase, respectively, as is found in liquid–liquid countercurrent distribution. The variation of efficiency with time and temperature of injection of liquid samples illustrates that an important requirement for high efficiency is the rapid vaporization of the sample. The more rapid the vaporization, the narrower is the width of the zone travelling through the column and the higher the efficiency. Also, injection of liquid samples at for example room temperature, which can vary appreciably from day to day, may affect quantitative analysis even with an internal standard if a method such as comparison of peak heights is used. The rate of change of peak height of an internal standard with temperature of injection may be significantly different from the rate of change of height of the peaks being analysed. This was shown for chloro-methanes when acetone was used as the internal standard[6].

The authors wish to thank the National Smelting Company, Avonmouth, and the Imperial Chemical Industries Ltd, for samples of halogenated hydrocarbons. One of them (C. J. H.) thanks Messrs British Celanese Ltd for a Senior Research Studentship during the tenure of which the above work was carried out.

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11

DETECTION OF VAPOURS IN FLOWING GAS STREAMS

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At this stage in the development of gas–liquid chromatography it is perhaps worthwhile to examine the methods of vapour detection used to date, and to suggest what seem to the author and Martin to be profitable lines for future study.

The conditions which should be fulfilled ideally by a method of detection of vapours in gas streams are the following.

(*1*) The technique should preferably be applicable to all substances irrespective of their chemical nature. Subsidiary techniques capable of selectively detecting specific chemical structures (double bonds, hydroxyl groups, etc.) can on occasion provide all the required information though the mixture to be analysed contains too many substances of other chemical types for complete resolution by any general method.

(*2*) The apparatus should be relatively simple and easily constructed.

(*3*) Sensitivity should be high so that (*a*) very small amounts may be detected, (*b*) the chromatogram loads may be kept low so that ideal behaviour may be obtained, and (*c*) lower column temperatures may be used with consequent gains in the separation factors.

(*4*) The internal volume of the detector should be as small as possible to avoid loss of resolution by the mixing within the apparatus of substances already separated on the column.

(*5*) The detector should not absorb appreciable quantities of vapour from the gas stream, thus its temperature should preferably be not less than that of the column.

(*6*) The response of the apparatus should be dependent on some simple law so that the instrument would not require calibration for each and every substance and set of conditions. A linear response only becomes of importance when accurate quantitative results are required.

(*7*) The results should be capable of being recorded automatically.

(*8*) The instrument should be insensitive to changes in rate of flow of gas and also to changes of temperature.

(*9*) Instruments are required to record both the instantaneous concentration and also the total mass (or some function of mass) of the material emerging from the column. It should be noted that a machine which records the total mass by integrating a measurement of instantaneous concentration will not in general give so accurate a value of total mass as an instrument which measures this directly, since uncertainty of the zero of concentration will give rise to cumulative error in the former.

The recording of the instantaneous concentration of material in the gas stream possesses the following advantages.

(*a*) It is easy to find the position of the centre of the emerging zone, a factor of some importance where identification depends on accurate knowledge of the time of emergence of the zone.

(*b*) A composite peak is more easily seen in such a record than in a recording of the total mass of material emerging from the column.

(*c*) It is easier to notice very small peaks.

The recording of the total mass of material emerging from the column, however, possesses one great advantage, quantitative estimation necessitates only the measurement of the step height and not the time-consuming measurement of zone area necessary in the former type of recording.

Present Methods

(*1*) *Titration*

Automatic titration of ionizable substances is attractive because of its simplicity and provision of direct quantitative results, but has obvious limitations.

(*2*) *Thermal conductivity*

The katharometer is essentially a simple piece of apparatus to construct, but possesses a number of disadvantages.

(*a*) It is sensitive to changes in rate of gas flow though this can be countered to some extent by the use of self-purging cells of the type described by Dimbat *et al.* (1956).

(*b*) This sensitivity to flow rate does not allow the columns to be loaded by interrupting the carrier gas flow and placing the sample directly on the packing. Injection techniques are necessary and in unskilled hands can lead to spreading the material over too large a volume of inlet gas with consequent impairment of separation.

(*c*) The sensitivity of many katharometers is not quite high enough to allow detection of minor components of mixtures without overloading of the column and its attendant loss of resolving power.

(*d*) Contact between the vapour being detected and the hot sensing element can occasionally lead to decomposition on the wire and the production of spurious signals.

(*e*) It is often necessary to calibrate for each component of a mixture.

Nevertheless, the simplicity of the apparatus has ensured its use by a number of workers. However, as Martin has already pointed out, it should be possible to increase sensitivity by working the cell at a pressure of a few millimetres of mercury so that very small columns could be used with loads of a few microgrammes. No work along these lines has yet been reported.

(*3*) *The gas density meter*

This instrument invented by Martin has the great advantage of following a simple parameter, molecular weight. Because of this, quantitative results are obtained by the simplest of calibrations. Response is linear up to quite high concentrations and its sensitivity is extremely high. It is more difficult to make than the katharometer, but by no means as difficult as many have

supposed. Accurate temperature control is necessary for the maximum zero stability, and vapour heating is consequently necessary. The materials being detected do not come into contact with surfaces any hotter than the columns themselves.

(4) *Volume measurement*

The elegant technique developed by Janák of using an absorbable carrier gas so that the volume of residual gases can be measured directly is most attractive. It is limited in scope, however, to the lower hydrocarbons and permanent gases. Sensitivity is not very high at its present stage of development, but the method could readily be made self-recording.

(5) *Flow impedance methods*

These techniques introduced by Phillips and his school are relatively simple, but require very accurate control of flow rate and detailed calibration.

(6) *Destructive methods*

Two such methods have been developed. In the first, the gas stream from the chromatogram is passed over heated copper oxide where carbon-containing substances are oxidized and the resultant carbon dioxide determined with a commercial infra-red detector. The method is sensitive, but somewhat cumbersome, and is limited, of course, to carbon compounds. It has a further disadvantage that the materials from the chromatogram are destroyed.

The second method, invented by Scott, burns the separated materials in a hydrogen flame where temperature is followed by means of a thermocouple placed above the flame. This is another elegant and simple method that would repay further study. From many points of view, however, destruction of the separated materials is a great drawback.

(7) *Vibrating reed electrometer*

This device developed by Phillips and his school is exceptionally sensitive towards some substances, but is limited in applicability and often slow in response. Nevertheless, for specific separations it can be most useful.

(8) *Some possible methods*

It is not my intention to do more than sketch briefly some ideas that Martin and I had thought promising.

First, ionization. It should be possible to detect vapours by taking advantage of the change in ionization potential of the gas stream. Sensitivity should be high, but calibration for each substance would be required.

Secondly, viscosity. A differential viscometer of roughly similar type to that used for liquids could be used to compare viscosities of carrier gas and chromatogram gas. This method could be adapted to produce an integrated signal making quantitative measurements easy.

Thirdly, and perhaps the most attractive, is the measurement of sound velocity in the gas. This parameter is dependent on density and hence on molecular weight, so that quantitative results are more easily obtainable. The difference in sound velocity between reference and chromatogram streams is such that high sensitivity is possible without too great elaboration,

a pulse technique being the most attractive. The phase shift method described by Lawley and incorporated in a commercial instrument has low sensitivity for this purpose and the cell has a large dead-volume.

Fourthly, radioactivity. Where radioactive substances are being separated it would be a great convenience to couple a Geiger–Müller or proportional counter capable of operating at column temperatures, to a detector such as the katharometer or the gas density meter. In this way a combination of counting and concentration recording is achieved so that the specific activities of the substances separated could be directly determined.

Techniques involving light absorption, interferometry or measurement of dielectric constant are unlikely ever to attain high sensitivities, but might well be useful for preparative scale elution chromatograms or for displacement analysis.

The field is open for the development of more sensitive and simpler detectors, and it is to be hoped that workers in the field will not rest content with the instruments at present available.

NOTE: For Discussion see pages 162–168, where Chapters 11–14 are treated together.

12

A NEW DETECTOR FOR VAPOUR PHASE PARTITION CHROMATOGRAPHY

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A new detector is described for application in vapour phase partition chromatography using hydrogen or a gaseous mixture containing hydrogen as a carrier gas. The method of detection depends on the measurement of the flame temperature of the exit gas when burnt at a small jet. This apparatus will detect quantitatively 2 μg of benzene at a concentration of 0·1 μg of vapour per millilitre of carrier gas. The detector is particularly applicable to hydrocarbon analyses. The area of any peak of a chromatogram, corrected for the heat of combustion of the substance, is proportional to the weight present. A complete quantitative analysis can be obtained without knowledge of the original weight of the charge.

Partition chromatography in the vapour phase has been developed as a valuable technique for the analysis of mixtures of hydrocarbons or other volatile materials[1–3]. Two detectors are being used, the vapour density bridge[1] and the thermal conductivity cell[2]. The application of an infra-red carbon dioxide detector to this problem has also been reported[4]. The vapour density bridge has an excellent sensitivity but is rather difficult to construct, whereas the thermal conductivity cell is relatively simple to make but is somewhat less sensitive. The flame detector described here has a high sensitivity and a simple form is made readily in any workshop. It also has particular application in high temperature vapour phase chromatography as its stability can be maintained up to 300°C. The flame detector is used with hydrogen or a gaseous mixture containing hydrogen as a carrier gas.

The method of detection is based on the measurement of the temperature of the flame, when the exit gas is burnt at a small jet. When an organic vapour is present in the exit gas, the flame lengthens and engulfs a thermocouple placed slightly above the normal flame. The change in temperature of the thermocouple appears to depend mainly on the heat of combustion of the substances present. An important advantage is that the detector can be made with a very small dead-space between the column and the jet. Two forms of the detector are described, the simple form suitable for experimental work and the more involved type suitable for routine analysis or other regular use. Due to the low cost of the flame detector, several columns with various liquid phases running at different temperatures can be constructed, each with its own detector. Thus, a suitable column for the analysis required can always be available for immediate use. The materials required for the simple type of detector are normally available in any laboratory and a complete vapour

phase chromatographic apparatus can be constructed in a few days. Quantitative chromatograms may then be obtained with 2-mg samples by hand plotting from the readings on an ordinary spot-galvanometer. The modified type of detector, though not costly, needs more skill in construction. It is very suitable for permanent equipment for use up to 300 C.

Description of Apparatus using Simple Detector

A diagram of the complete apparatus is shown in *Figure 1*. The partition column is four feet in length, bent in the form of a U, and is thermostatted

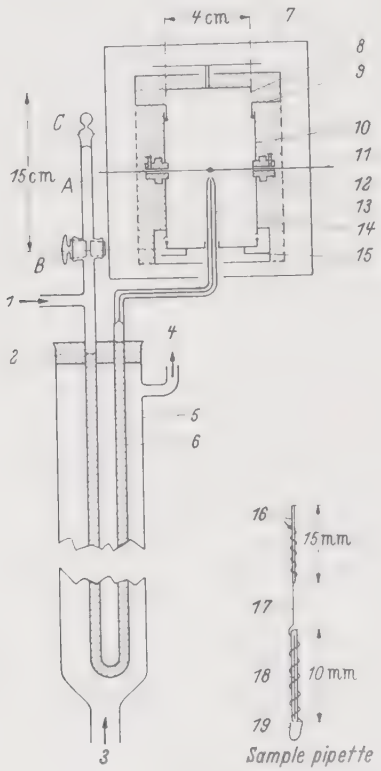

Figure 1. Apparatus using simple detector

1, Hydrogen supply from flowmeter and constant pressure device; 2, Rubber bung; 3, Solvent vapour from boiler; 4, To condenser; 5, Vapour jacket; 6, Partition column containing Celite and liquid phase; 7, Loose-fitting box to to exclude draughts; 8, Baffle plates; 9, Asbestos wool insulator; 10, Metal housing; 11, Thermocouple leads; 12, Insulated thermocouple supports; 13, Thermocouple junction; 14, Glass capillary jet; 15, Baffle plates; 16, Iron wire; 17, Copper fuse wire; 18, Glass capillary; 19, Wire guard

with vapour from a solvent boiling at a suitable temperature. The sample pipette, shown in *Figure 1*, is charged with 1·5–2 mg of sample by the surface tension effect when the tip of the capillary is dipped into the liquid. The pipette is dropped into tube *A*, and stopper *C* replaced and tap *B* opened. The pipette falls on to the column packing and is discharged on to the column, again by the surface tension effect. The pipette is then withdrawn into *A* by the action of a magnet on the piece of iron wire attached to the capillary. Tap *B* is closed and the pipette removed.

The thermocouple in the detector may be made of platinum/platinum + 14 per cent rhodium, palladium–gold/platinum–iridium or iron/constantan. The last, although used outside its normal practical range, has proved most

effective; it appears to give the highest overall sensitivity and the most constant zero. The thermocouples used are made from 32 s.w.g. (0·274 mm diameter) iron and constantan wire, brazed together with a silver bronze alloy, m.pt 875 °C, leaving a globule of alloy at the junction about 1·5 mm in diameter. This metal globule increases the thermal inertia of the couple and

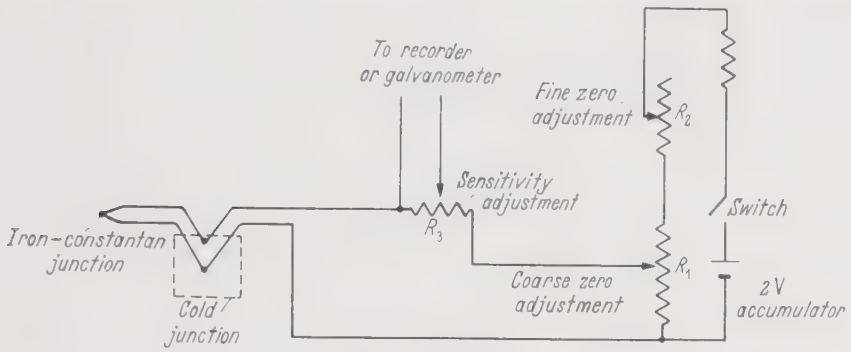

Figure 2. Potentiometer circuit

results in greater zero stability. The jet is made of Pyrex glass capillary tubing and has a bore of about 0·2 mm. It must be fixed rigidly to the base of the detector housing if quantitative results are required. For the same reason, the thermocouple must be mounted rigidly, because the distance

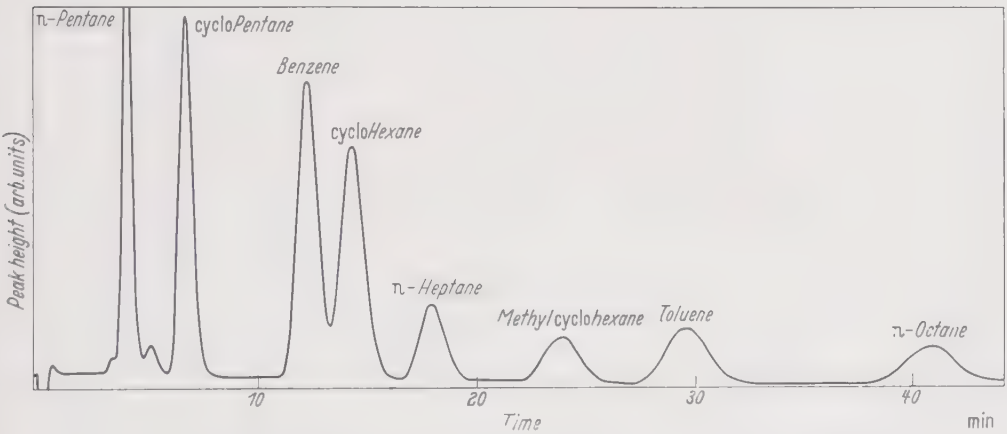

Figure 3. Chromatogram of a synthetic mixture using the simple detector

Gas composition: 25% nitrogen, 75% hydrogen
Gas flow rate: 40 ml/min
1·3 µl *charge. Temperature* 78°C
Chart speed: 0·5 inch/min
Thermocouple ht: 2 mm

between the jet and the thermocouple affects the sensitivity of the detector. The detector incorporates a number of baffle plates that are essential to reduce the effects of draughts. When working at maximum sensitivity, it is advisable to wrap the housing in asbestos wool and enclose the whole detector in a box to exclude draughts completely. The thermocouple wires pass from the detector to a thermally insulated cold junction and thence to a

simple potentiometric network (*Figure 2*) constructed from ordinary wire-wound radio potentiometers and leaf-type switches. The output from this circuit can be fed to a spot-galvanometer and chromatograms obtained by hand-plotting, or alternatively fed to a 0·5 or 1·0 mV potentiometric recorder.

Method of Operation

Hydrogen or a mixture of hydrogen and nitrogen from a constant-pressure supply is adjusted to the required rate of flow and ignited at the jet. After allowing a few minutes for equilibrium to become established, the potentiometer accumulator is switched on and the galvanometer adjusted to zero with resistances R_1 and R_2 (*Figure 2*). The sensitivity is then set at the required value with the resistance R_3, the sample is introduced into the column and the chromatogram recorded. Part of a typical chromatogram obtained for a mixture of *n*-pentane, *cyclo*pentane, benzene, *cyclo*hexane, *n*-heptane, methyl*cyclo*hexane, toluene and *n*-octane is shown in *Figure 3*.

Characteristics of the Detector

1. Sensitivity

The characteristics of the detector were investigated using a 4-ft column carrying 18 per cent white petroleum oil (liquid paraffin) on Celite at a temperature of 78 C. A hydrogen flow rate of 48 ml/min was used and the overall instrument sensitivity was adjusted so that the zero instability was less than 1 per cent of the full-scale deflection. A 5 per cent by weight solution of benzene in toluene was successively diluted with toluene until the benzene peak for a 2-mg sample was 2 per cent of full-scale deflection. The weight of

Table I. Measurement of Peak Height

Detail	cyclo*Pentane*	*Benzene*	n-*Heptane*
Peak height in arbitrary units	2·88 2·92 2·92 2·91 2·86 2·80 2·89 2·88 2·86 2·88	2·01 2·06 2·11 2·07 2·02 1·95 2·01 2·01 2·00 1·99	2·15 2·20 2·24 2·19 2·13 2·04 2·15 2·21 2·12 2·10
Standard deviation *Repeatability*[5]	0·033 0·107	0·043 0·137	0·056 0·180
Repeatability expressed as % w/w of hydrocarbon in mixture	1·25	2·03	3·35
Approximate composition of mixture % w/w	30	30	40
Retention volume ml	174	320	500

benzene in this sample, which was taken to be a measure of the sensitivity of the detector, was found to be equivalent to 2 μg of benzene. This corresponds to a concentration of 0·1 μg of benzene per millilitre of hydrogen. Thus with a 2-mg charge as little as 0·1 per cent of benzene could be detected easily.

2. Measurement of peak height

The determination of the precision of peak-height measurements for a given charge of sample was carried out under the same column conditions as described in section 1, with the exception that the overall sensitivity of the

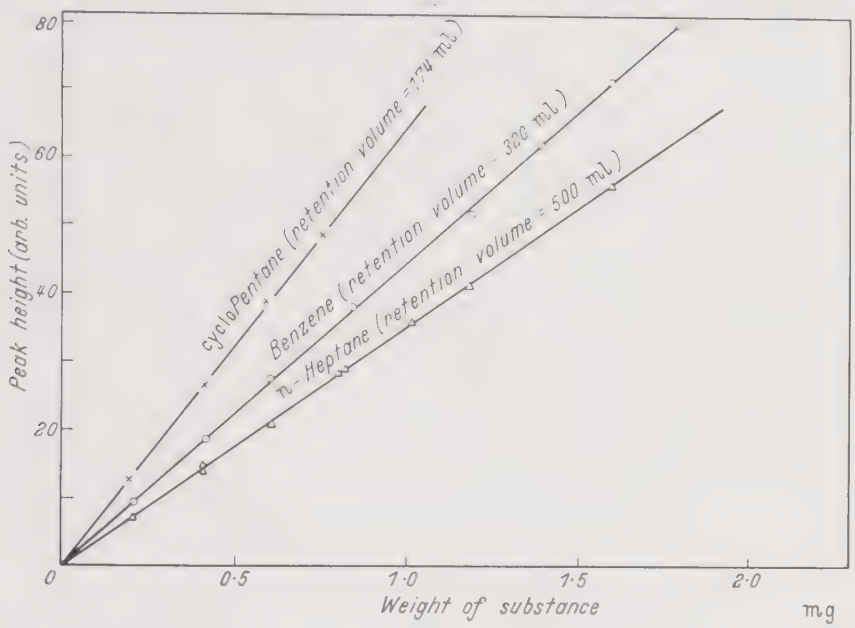

Figure 4. Relationship between peak height and weight of substance

detector was reduced to 5 per cent of the maximum. Two-milligramme samples of a mixture of 30% w/w *cyclo*pentane, 40% w/w *n*-heptane and 30% w/w benzene were used and ten replicate chromatograms were obtained. The peak heights were taken as the distance between the peak maximum and the mean of the two minima. The difference between the minima on either side of the peak was rarely more than 1 per cent of the full-scale deflection. The results are shown in *Table I*, in which the precision is given in terms of repeatability as defined by the Institute of Petroleum[5].

3. Relationship between peak height, peak area and weight of charge

Chromatograms were obtained, using the same conditions as in the determination of repeatability, for 2-mg samples of nine different mixtures of *cyclo*pentane, benzene and *n*-heptane. Each mixture was chromatographed in duplicate and the peak heights were measured in the manner described above. Results are shown in *Figure 4*. Similar results were obtained for the C_5 C_8 *n*-paraffins and the peak heights were plotted against weight of substances (*Figure 5*). Peak areas were also measured.

4. Relationship between individual peak areas and the total area of the chromatograms

Three different hydrocarbon mixtures, each containing three naphthenes, three paraffins and two aromatics, were chromatographed in duplicate under the same conditions as described in section 2. A weight of paper, equivalent to each peak area, was obtained by reproducing it on tracing paper, cutting it out and weighing the piece of paper. Each weight, expressed as a percentage of the total weight of all the peaks in the chromatogram, was taken to represent the percentage by weight of the component in the mixture. The results obtained are shown in *Table II*.

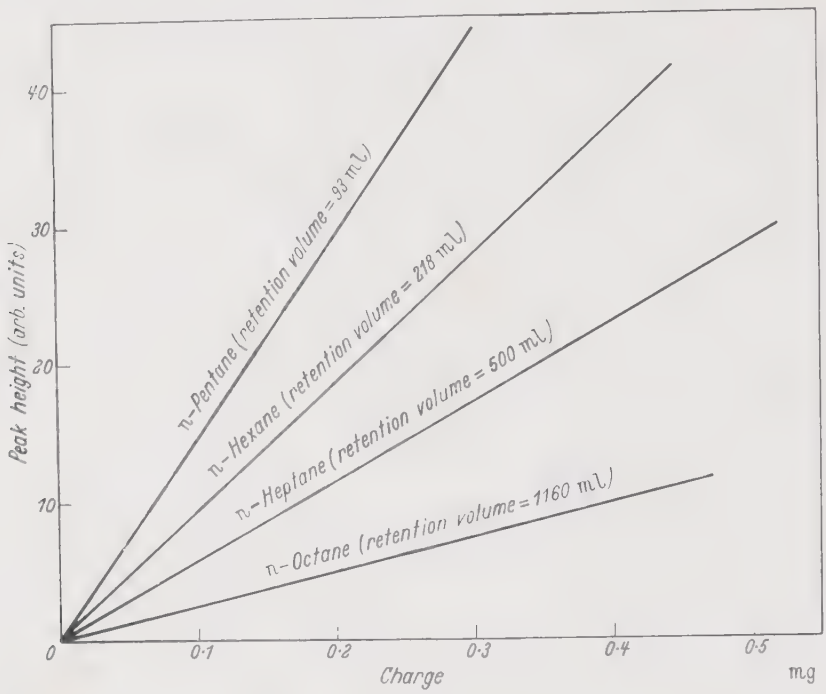

Figure 5. Relationship between peak heights and weight of charge on column for a series of n*-paraffins*

Review of Results

In most of the experiments described in this paper, a mixture of 75 per cent hydrogen and 25 per cent nitrogen was used, as this was found to give a higher column efficiency with the method used for packing the column.

The results obtained from the determination of the precision of peak heights for a given charge show that the greater the retention volume the greater the error of measurement (*Table I*). This is to be expected, as the peak height for a given weight of substance rapidly decreases along the chromatogram, due to the effect of diffusion in the gaseous and liquid phases during passage down the column. *Figures 4* and *5* show that the relationship between the peak height for a single substance and the weight of the substance present is linear and that the slopes of the lines for different compounds decrease with increasing retention volume. However, the results for *cyclo*pentane, benzene and *n*-hexane show that by plotting peak areas against the weight of substance

Table II. Composition of Mixtures Determined from Relative Peak Areas

Substance	Blend 1 (% w/w)				Blend 2 (% w/w)				Blend 3 (% w/w)			
	Determined			Actual	Determined			Actual	Determined			Actual
	(1)	(2)	Mean		(1)	(2)	Mean		(1)	(2)	Mean	
n-*Pentane*	11·0	10·9	11·0	12·2	8·3	8·7	8·5	9·0	14·8	14·8	14·8	13·9
cyclo*Pentane*	7·0	7·1	7·1	8·2	7·5	8·6	8·0	8·8	15·3	15·5	15·4	16·0
Benzene	12·2	12·4	12·3	12·9	10·7	10·7	10·7	11·9	23·2	22·6	22·9	22·8
cyclo*Hexane*	15·7	16·5	16·1	16·5	16·6	16·0	16·3	16·6	10·1	10·0	10·0	9·6
n-*Heptane*	15.2	14·5	14·8	13·0	14·5	13·7	14·1	12.4	9·3	9·6	9·5	8·7
Methylcyclohexane	15·8	16·7	16·2	15·1	15·0	16·0	15·5	14·9	13·5	13·9	13·7	8·7
Toluene	11·5	10·9	11·2	11·7	15·2	14·2	14·7	14·9	7·7	7·9	7·8	13·7
n-*Octane*	11·6	11·0	11·3	10·4	12·2	12·1	12·2	11·5	6·1	5·7	5·9	6·6
Total	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0

Table III. Composition of Mixtures Determined from Relative Peak Areas, Corrected for Heats of Combustion

Substance	Heat of combustion kcal/g	Blend 1 (% w/w)			Blend 2 (% w/w)			Blend 3 (% w/w)		
		Mean det.	Corrected for heat of combn	Actual value	Mean det.	Corrected for heat of combn	Actual value	Mean det.	Corrected for heat of combn	Actual value
n-*Pentane*	11·63	11·0	10·4	12·2	8·5	8·0	9·0	14·8	13·9	13·9
cyclo*Pentane*	11·20	7·1	7·0	8·2	8·0	7·8	8·8	15·4	15·0	16·0
Benzene	10·02	12·3	13·5	12·9	10·7	11·7	11·9	22·9	24·9	22·8
cyclo*Hexane*	11·43	16·1	15·5	16·5	16·3	15·7	16·6	10·0	9·5	9·6
n-*Heptane*	11·17	14·8	14·6	13·0	14·1	13·9	12·4	9·5	9·3	8·7
Methylcyclohexane	11·14	16.2	16·0	15·1	15·5	15·3	14·9	13·7	13·4	13·7
Toluene	10·15	11.2	12·1	11·7	14·7	15·9	14·9	7·8	8·4	8·7
n-*Octane*	11·42	11·3	10·9	10·4	12·2	11·7	11·5	5·9	5·6	6·6

present, a single straight line is obtained for all three hydrocarbons (*Figure 6*). This is due to the fact that the calorific values per gramme of the hydrocarbons were similar. James and Martin[1] and also Littlewood, Phillips and Price[1] found linear relationships between peak areas and weight for given substances but the constant of linearity differed for each substance.

The results show that quantitative values can be obtained from a chromatogram by relating the peak areas of individual peaks to the total area of all the peaks obtained (*Table II*). It is seen that results obtained for the synthetic mixtures differ by only about 2 per cent from the actual values, but that this

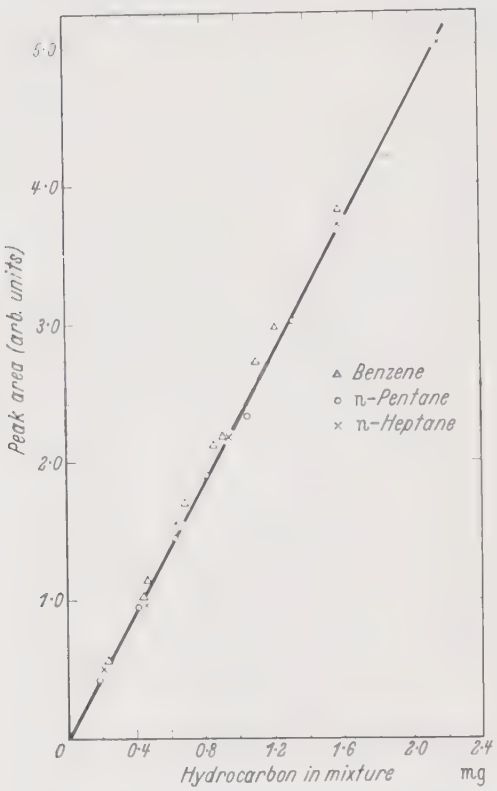

Figure 6. Relationship between peak area and weight of substance

difference is not due merely to experimental error. *Table III* shows the values obtained corrected for differing heats of combustion of the substances concerned. This correction has been found to be effective for substances with widely differing heats of combustion, e.g. hexane and thiophen. However, it does not bring the results for hydrocarbons much closer to their actual values, because their calorific values per gramme do not vary greatly from one to another.

Description of Apparatus for Routine Analysis

A diagram of the apparatus is shown in *Figure 7*. It is made entirely of brass, except for the column tube itself, and all joints are made with high melting-point solder. The jacket for the detector and the column and the boiler consist of one length of 3-inch diameter brass tubing, which is bolted to a

flange carrying the detector housing. The partition column consists of 5 ft of $\frac{1}{4}$-inch external diameter copper tube bent in the form of a U, one end of which is joined to the base of the detector housing by means of a brass union. The other end of the column fits into another brass union, soldered to the flange. This arrangement allows the column to be removed easily and re-packed if required. An injection system, similar to that used with the simple

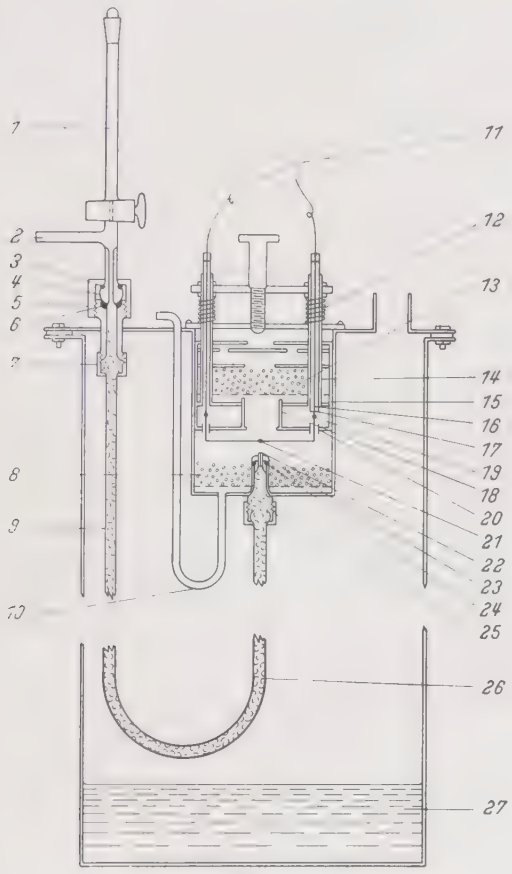

Figure 7. Apparatus for routine analysis

1, Injection system; 2, Gas supply; 3, Teflon washer, 4, Male spherical joint; 5, Brass union; 6, Teflon washer; 7, Brass union; 8, Porcelain beads; 9, Copper partition column; 10, Air supply tube; 11, Leads from thermocouple; 12, Set spring; 13, Porcelain beads; 14, Stainless steel gauze; 15, Brass tube; 16, Copper wire; 17, Glass insulating tube; 18, Pyrex tube; 19, Cu/Au–Pd *cold junction; 20, Brass thermocouple assembly; 21,* Pd–Au/Pt–Ir *thermocouple; 22, Glass jet; 23, Copper ferrule; 24, Teflon washer; 25, Brass union; 26, Partition column; 27, Heating liquid*

detector, is attached to the column by means of a brass–glass union, an air-tight seal being achieved by means of a male, glass, spherical joint and a Teflon washer. The air supply to the detector is preheated by passage through a copper tube suspended in the thermostatting vapour and enters the base of the detector housing, where it is diffused through a bed of porcelain beads. This prevents any local currents of air displacing the hydrogen flame away from the thermocouple. The union at the base of the detector housing carries a length of copper tube that projects about $\frac{3}{4}$ inch into the housing and terminates in a copper ferrule. Inside this copper ferrule is sealed a Pyrex

jet. This jet has an aperture of about 0·2 mm and is sealed to the copper ferrule with silver chloride. A gas-tight joint between the copper ferrule and the copper tube is obtained with the aid of another Teflon washer. The thermocouple assembly consists of two hollow brass cylinders supported by brass tubes that slide through two holes in the brass flange. These tubes are held in position by two springs, acting on a cross-bar through which a bolt with a knurled head passes and presses on the upper surface of the flange. The thermocouple assembly, and thus the position of the thermocouple in respect of the flame, can be adjusted vertically by rotation of this bolt. The thermocouple leads, contained inside glass sleeves, pass through the two hollow brass cylinders via the supporting brass tubes. The thermocouple is made from 35 s.w.g. palladium–gold/platinum–iridium wires. The cold junctions are situated inside the lower brass cylinder and are protected from the hot gases by a short length of Pyrex tube. The burnt gases, after passing up the Pyrex tube, are diffused through another layer of porcelain beads supported on a stainless steel gauze in the upper brass cylinder. After traversing the upper brass cylinder, the gases escape through a simple baffle system to the atmosphere. The output from the thermocouple is fed to the same potentiometric network as that used with the simple detector. The method of operation of this apparatus is the same as that described for the simple detector, except that the gas is ignited by a spark from a magneto. The spark passes between the thermocouple and a subsidiary electrode. The electrode is attached to the base of the lower brass cylinder. The air flow is controlled by a separate reducing valve and is adjusted so that 50–100 per cent excess of oxygen is present for combustion. The apparatus can be run at temperatures up to 300 C and typical chromatograms obtained from this equipment are shown in *Figures 8* and *9*.

Sensitivity

The sensitivity of the apparatus was determined by the same method as that used for the simple detector. The column conditions used were as follows:

Column length	4 ft
Liquid phase	20% paraffin on Celite
Column efficiency to benzene [1]	800 theoretical plates
Gas composition	25% nitrogen, 75% hydrogen
Gas flow rate	40 ml/min
Air flow rate	500 ml/min
Chart speed	½ inch/min
Distance between thermocouple and jet	1 mm
Column temperature	78°C
Total charge	1·7 μl

The apparatus was adjusted so that the zero drift was less than 1 per cent of full-scale deflection and it was found that 1·1 μg of benzene gave a peak height of 2 per cent of full-scale reading. This value of 1·1 μg was taken as the maximum sensitivity of the apparatus and is equivalent to an average concentration 0·05 μg of benzene per millilitre of carrier gas.

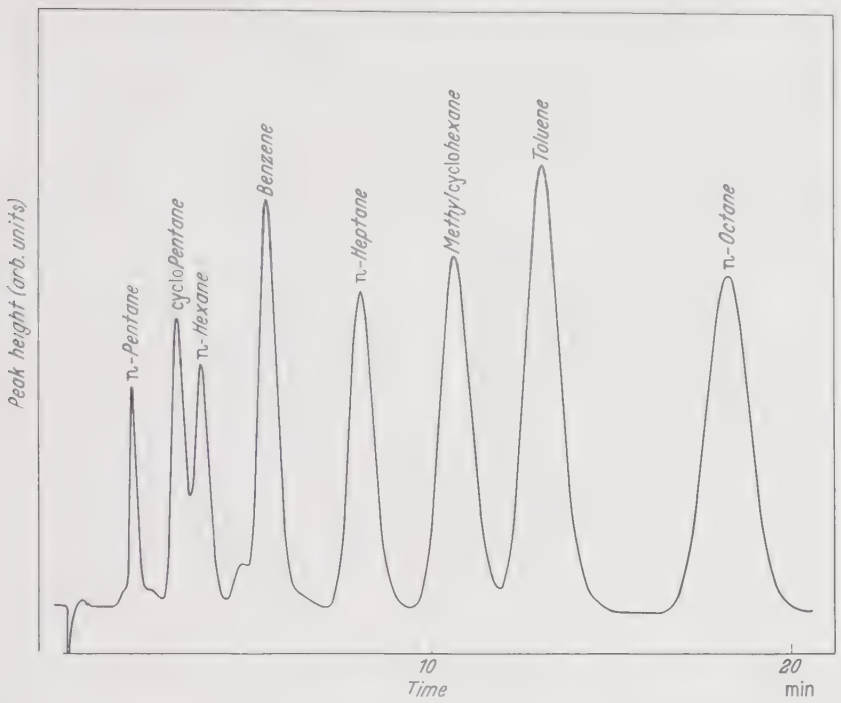

Figure 8. Typical chromatogram of a hydrocarbon mixture

Column No. 2. Length 4 ft; 20% *paraffin on Celite.*
Gas composition: 25% *nitrogen;* 75% *hydrogen.*
Gas flow rate: 40 ml/min. *Chart speed:* 0·5 inch/min
Air flow rate: 500 ml/min. *Thermocouple ht:* 3·5 mm
Temperature 78°C. *Injection:* 3·7 μl

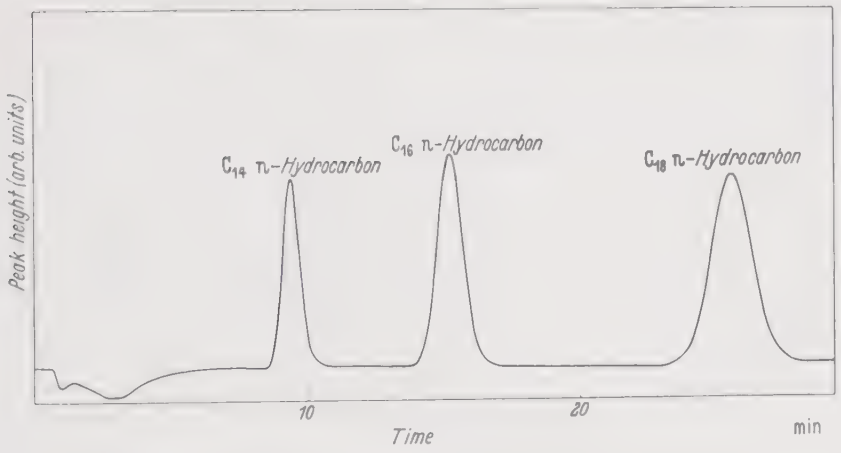

Figure 9. Typical chromatogram of a hydrocarbon mixture

Column No. 6. Length 4 ft. 20% *Apiezon L on Celite.*
Hydrogen flow rate: 50 ml/min. *Air flow rate:* 500 ml/min
Chart speed: 0·5 inch/min. *Thermocouple ht:* 3·5 mm.
Temperature: 290°C. *Injection:* 2·5 μl

Quantitative Response at 78°C

The quantitative response of the apparatus was determined by analysing the following five synthetic mixtures:

Mixture 1

Carbon disulphide	7·6% w/w
Benzene	20·6% w/w
Trichlorethylene	26·0% w/w
Toluene	45·8% w/w

Mixture 2

Dichlorethylene	15·2% w/w
n-Heptane	25·1% w/w
Methyl*cyclo*hexane	39·4% w/w
2-Methyl thiophen	20·3% w/w

Mixture 3

Benzene	19·2% w/w
n-Heptane	39·7% w/w
Methyl*cyclo*hexane	24·8% w/w
Toluene	16·3% w/w

Mixture 4

n-Pentane	17·5% w/w
*cyclo*Pentane	25·8% w/w
Benzene	56·7% w/w

Mixture 5

Benzene	98·43% w/w
n-Heptane	0·63% w/w
Methyl*cyclo*hexane	0·26% w/w
Toluene	0·48% w/w

Mixtures 1 and 2 were designed to indicate the quantitative response of the apparatus to compounds of different classes, present in different concentrations. Mixtures 3 and 4 were designed to show the behaviour of the apparatus to different classes of hydrocarbons at different concentrations, while Mixture 5 demonstrated the application of the detector to determine traces of hydrocarbons present in an almost pure compound. Mixtures 1, 2, 3 and 4 were chromatographed in duplicate, using the same column conditions as in the determination of sensitivity.

The areas of the peaks obtained from each chromatogram were corrected for heat of combustion, and each corrected peak area was expressed as a percentage of the total corrected area of all the peaks in the chromatogram. The results obtained are shown in *Table IV*. It may be seen that an average difference between the mean and the actual value for a given component is 0·8 per cent, the maximum difference being about 2 per cent.

Five replicate chromatograms were obtained for Mixture 5, again using the same column conditions but with 2·5-mg injections. The results, however, were calculated somewhat differently. It was assumed that 0·63% w/w of *n*-heptane was present and the percentage of methyl*cyclo*hexane and toluene calculated by comparing the respective corrected peak areas with that for *n*-heptane. The results obtained (*Table V*) show that substances, present at a concentration of 1 per cent or less, can be determined by comparing peak areas with that of an added, known standard.

Table IV. Quantitative Analysis of Synthetic Mixtures

Substance	*Calorific value* kcal/g	*Column efficiency* theoretical plates	*Retention volume* ml	% w/w *Determined* (*1*)	(*2*)	*Mean*	*Actual*
Carbon disulphide	3·33	690	136	6·6	7·4	7·0	7·6
Benzene	10·11	660	248	20·1	21·2	20·7	20·6
Trichlorethylene	1·60	720	340	25·6	25·0	25·3	26·0
Toluene	10·22	1100	600	47·7	46·4	47·0	45·8
				100·0	100·0	100·0	100·0
Dichlorethylene	2·74	625	184	14·7	13·2	14·0	15·2
n-*Heptane*	11·55	850	368	23·2	25·2	24·2	25·1
Methylcyclohexane	11·20	900	492	39·8	40·4	40·1	39·4
2-Methylthiophen	8·45	1060	596	22·3	21·2	21·7	20·3
				100·0	100·0	100·0	100·0
Benzene	10·11	1000	260	18·7	19·5	19·2	19·2
n-*Heptane*	11·55	1150	380	37·9	37·1	37·5	39·7
Methylcyclohexane	11·20	1000	500	25·2	25·7	25·4	24·8
Toluene	10·22	1100	610	18·2	17·7	17·9	16·3
				100·0	100·0	100·0	100·0
n-*Pentane*	11·61	480	190	15·5	15·3	15·4	17·5
cyclo*Pentane*	11·27	570	335	25·7	26·2	25·9	25·8
Benzene	10·11	900	645	58·8	58·5	58·7	56·7
				100·0	100·0	100·0	100·0

Quantitative Response at 300°C

Three mixtures of *n*-tetradecane, *n*-hexadecane and *n*-octadecane were chromatographed, using the following column conditions:

Column length	4 ft
Liquid phase	20% Apiezon L grease on Celite
Column efficiency to *n*-hexadecane[1]	1000 theoretical plates
Gas composition	100% hydrogen
Gas flow rate	40 ml/min
Air flow rate	500 ml/min
Chart speed	½ inch/min
Distance between thermocouple and jet	3·5 mm
Column temperature	298°C
Total charge	1·75 μl

The percentages of components were calculated in the manner previously described and the results are shown in *Table VI*. It can be seen that the quantitative response of the column is retained up to 300 C and excellent zero stability is maintained.

Table V. Quantitative Determination of Trace Components

Substance	% w/w						
	Determined						*Actual*
	1	*2*	*3*	*4*	*5*	*Average*	
Methylcyclohexane	0·36	0·34	0·34	0·33	0·31	0·33	0·26
Toluene	0·52	0·49	0·44	0·52	0·43	0·48	0·45

Table VI. Results from Quantitative Determinations

Substance	*Blend (1)*				*Blend (2)*				*Blend (3)*			
	% w/w *Determined*			% w/w *Actual*	% w/w *Determined*			% w/w *Actual*	% w/w *Determined*			% w/w *Actual*
	(1)	*(2)*	*Mean*		*(1)*	*(2)*	*Mean*		*(1)*	*(2)*	*Mean*	
n-*Tetradecane*	10·7	9·4	10·1	11·0	66·0	64·4	65·2	64·8	18·8	20·6	19·7	19·0
n-*Hexadecane*	67·4	68·1	67·7	68·0	9·4	9·2	9·3	9·5	32·8	33·3	33·0	32·7
n-*Octadecane*	21·9	22·5	22·2	21·0	24·6	26·4	25·5	25·7	48·4	46·1	47·3	48·3

The author wishes to thank the Directors of the National Benzole Company Ltd for permission to publish this paper, and Mr G. Matraves for his assistance in the experimental work.

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Note: For Discussion see pages 162–168, where Chapters 11–14 are treated together.

13

PROPERTIES OF THE MARTIN GAS DENSITY BALANCE AND POSSIBLE MODIFICATIONS THEREOF

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An electrical analogue of the system is described for evaluating performance. The theoretical results of modifications in design are discussed and some practical results of modifications are described.

The gas density balance devised by A. J. P. Martin is an ingenious and useful detector in gas chromatography. One of its outstanding advantages is that it measures a readily calculable property and hence does not need calibration for every new substance. Unfortunately there are very few published data on it, and indeed it seems that little quantitative study of the device, as such, has been done. The only reference in the literature appears to be a general article by A. T. James[1].

The objects of the present study were first the characteristics and limitations of Martin's original model, and secondly to find modifications which would not seriously impair the performance, but which would render construction easier and would also allow faults, such as leaks, to be more easily detected and remedied.

The Martin gas density balance is shown diagrammatically in *Figure 1*.

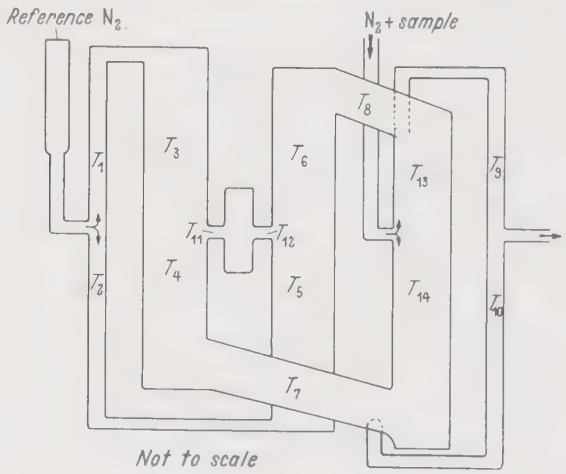

Figure 1. The Martin gas density balance

The tubes are drilled out of a solid copper block which is mounted in a vapour-jacketed case. The electrical equivalent circuit is shown in *Figure 2*.

The bridge arms are symmetrical and adjusted so that with nitrogen

flowing in the reference and sample sides there is no pressure drop across the anemometer.

Provided that the tubes are not horizontal, introduction of a heavier gas in T_{13} and T_{11} increases the pressure at the bottom of these tubes, causing a difference in pressure across the anemometer.

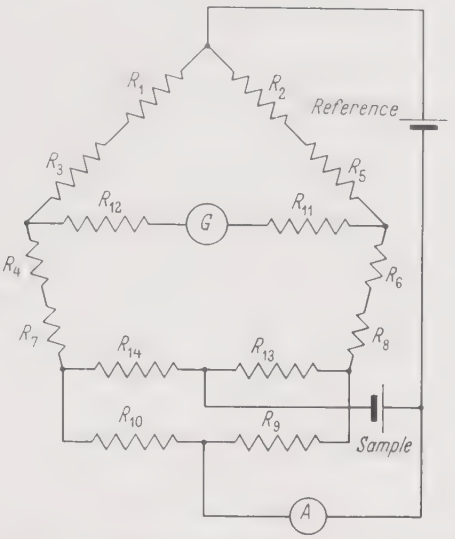

Figure 2. Electrical equivalent circuit of the Martin gas density balance

The resultant flow of gas through the anemometer gives an electrical signal which is recorded by a d.c. amplifier and self-balancing potentiometer system.

The Anemometer

The anemometer consists of a double thermocouple supported over a heater inside a hollow cylinder.

The temperature distribution in the cylinder was measured under static conditions (no pressure drop across the anemometer) by drawing a thermocouple at a steady rate through the anemometer and recording the output on a recording potentiometer.

The distribution under static conditions is shown in *Figure 3*(a). Rotation

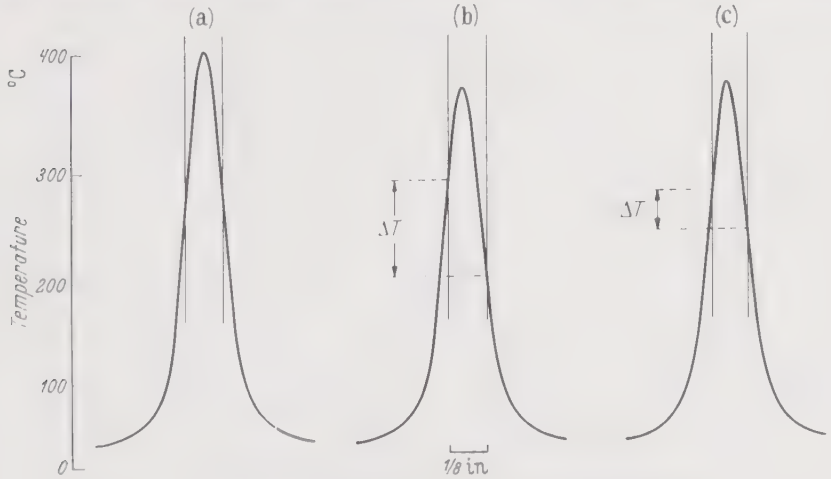

Figure 3. Temperature distribution across the anemometer

of the heater wire displaces the temperature maximum, as shown in *Figure 3*(b). Rotation of the heater may be used to balance the output from the two thermocouples. The balancing of the output in this way does not mean that the gas flow through the anemometer is necessarily zero.

The qualitative effect of gas flow in one direction is shown in *Figure 3*(c), where the maximum is displaced from its position in *Figure 3*(b) in the direction of flow.

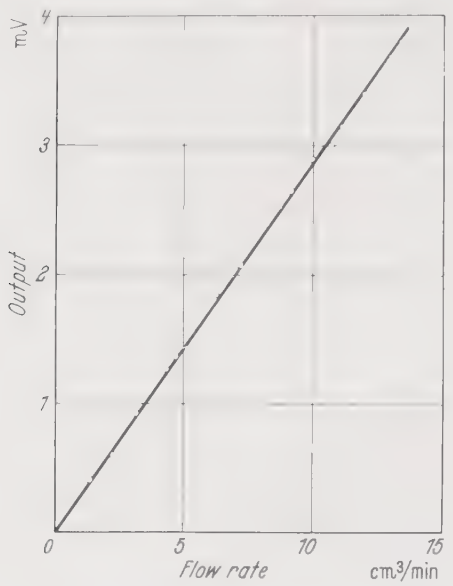

Figure 4. Relation between gas flow across anemometer and electrical output

To obtain a linear relation between the electrical output of the anemometer and the density change in T_{13} and T_{14}, the following conditions must be fulfilled.

(*1*) The pressure drop across the anemometer must be proportional to the density change

(*2*) The flow in the anemometer must be proportional to the pressure drop. This is true if the pressure drop is small in comparison with the pressure of the reference gas, provided that the resistance of the anemometer is constant

(*3*) The electrical unbalance resulting from the displacement of the temperature maximum must be proportional to the flow.

A graph of the measured relation between gas flow and electrical output is shown in *Figure 4*.

Variation in Sensitivity of Anemometer with Temperature

A pressure difference dp across a tube of radius a cm, length l cm, causes a gas flow of

$$Q = (p\ \mathrm{d}p/8\eta l)\pi a^4\ \mathrm{cm}^3/\mathrm{sec}$$

The viscosity η will increase as the square root of the absolute temperature so that the pressure difference dp corresponding to a density change δd produces a smaller gas flow through the anemometer as the temperature rises.

In addition the thermal conductivity of the gas in the anemometer also

increases, reducing the thermal gradients in the anemometer and causing a further reduction in sensitivity. The actual observed decrease in sensitivity of the balance with increase in temperature is shown in *Figures 8* and *9*.

To find the order of magnitude of the gas flow through the anemometer corresponding to the stated limit of detection of the balance (1 mole of amyl alcohol in 50,000 moles of nitrogen) a simple electrical analogue (*Figure 2*) was used. A system of pneumatic units can be defined after M. J. E. Golay[2].

Pneumatic Ohm: The pneumatic resistance across which a pressure of 1 dyne/cm^2 is developed by a gas flow of 1 cm^3/sec. The pneumatic resistance of a cylindrical tube of length l and radius a to a gas of viscosity η is

$$R = 8\eta l/\pi a^4$$

Pneumatic Ampere: A gas flow of 1 cm^3/second

Pneumatic Volt: A pressure of 1 dyne/cm^2

Pneumatic Farad: A capacitance into which an incremental pressure of 1 dyne/cm^2 causes an admission of 1 cm^3 of gas. The pneumatic capacity of a volume v of gas is v/p when v is in cm^3 and p is in dyne/cm^2.

The pneumatic resistances and capacitances of each tube in an actual balance are given in *Table I*.

Table I

Tube No.	*Pneumatic resistance*	*Pneumatic capacitance* μF
T_1	1·44	1·45
T_2	1·38	1·39
T_3	0·073	4·67
T_4	0·056	3·63
T_5	0·071	4·53
T_6	0·063	4·07
T_7	0·043	2·79
T_8	0·038	2·54
T_9	1·128	1·14
T_{10}	1·128	1·14
T_{11}	0·884	0·014
T_{12}	0·884	0·014
T_{13}	0·055	3·56
T_{14}	0·063	4·05

A resistance network with these values was constructed (*Figure 2*), and the total current through the system adjusted to 1·33 A corresponding to 80 cm^3/min gas flow. A voltage corresponding to an increase in density in the sample tube of 1 mole of amyl alcohol in 50,000 moles of nitrogen was injected at the junction of R_7 and R_{14}. (A low resistance thermocouple heated to the required temperature was used.) The change in the current passing through the anemometer resistance was measured.

It was estimated that a change in density corresponding to the addition of 1 mole of amyl alcohol to 50,000 moles of nitrogen would cause a change in gas flow through the anemometer of the order of 0·5 cm^3/hour.

A soap bubble flowmeter was then constructed which could measure rates from 0·1 cm^3/hour to 5 cm^3/min.

Air at varying rates was passed through an anemometer and the output plotted against flow rate. The results are shown on *Figure 4*.

The noise in the anemometer under static conditions is $\pm 1{\cdot}3$ μV.

Under dynamic conditions and a flow rate of 10 cm^3/hour the noise is ± 2 μV.

Onset of Turbulence in Anemometer

Temperature distribution curves in another anemometer were plotted with increasing gas flow through the tube. It was observed that at a flow rate corresponding to a density change of 0·12 ($N_2 = 1$) the curve became noisy [*Figure 3*(c)]. It is presumed that this was due to turbulence in the tube.

Experimental

Two models of the density balance were tested. One was made from a solid copper block and was very similar to Dr Martin's original design. The second was constructed entirely from copper tubing of the same internal dimensions

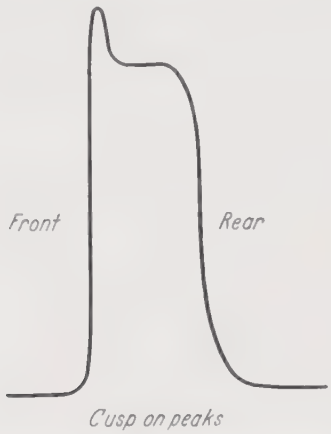

Figure 5. Peak showing a cusp at the front

as the tubes in the solid block. No provision for adjusting rods was made in the skeleton model, and they were not used in the solid block, the exit holes provided for them being merely stopped. The out-of-balance e.m.f. was small and was backed off by a potentiometer.

The two models were provided with kettle, vapour jacket, and column vapour jacket exactly as in Martin's original. The only modification made to the skeleton model was provision of means of circulating water through the jacket of the density balance if required.

A d.c. amplifier (noise $< 0{\cdot}3$ μV) and 5 mV Brown recorder were employed.

Two series of tests were carried out on each balance, one at room temperature and one at 56° C (acetone vapour jacket). At room temperature no thermostatting arrangements at all apart from the (empty) jacket and the heat capacity of the large mass of copper were employed. One experiment was done with tap water at 11° C circulating through the jacket of the skeleton balance.

A 7 mm column packed with kieselguhr plus half its weight of liquid paraffin was used in the sample side, with a similar column packed with plain kieselguhr in the reference side. The inlet pressure was 33·3 cm of mercury above atmospheric and the flow rates were 42 ml/min at 56° C and 53 ml/min at 20°C.

The tests were carried out with known mixtures of dry nitrogen (that used as a reference stream) and dry air or carbon dioxide; in one case pure argon was used as a sample. Samples were put into a by-pass loop of about 100 ml capacity and diameter about 7 mm in the supply line to the column. The pressure was adjusted to the inlet pressure before admitting the sample. The peaks obtained had a flat top, except for the 'cusp' (see above), for at least two thirds of their width indicating that the centre portion of each peak was caused by a gas of the made-up composition.

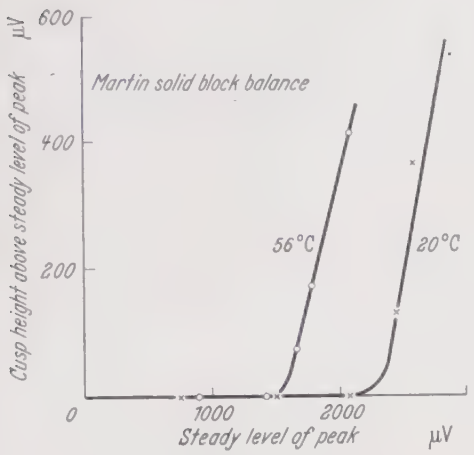

Figure 6. Effect of density difference on size of cusp (Martin)

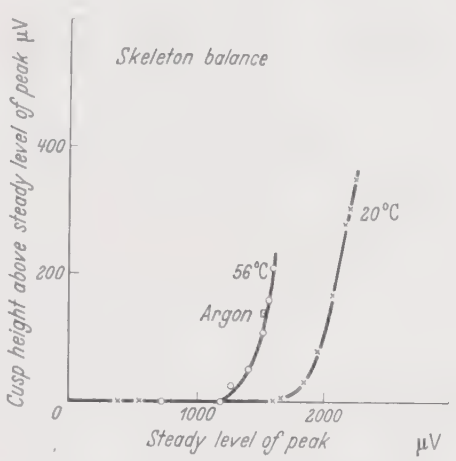

Figure 7. Effect of density difference on size of cusp (skeleton)

It was observed that above a certain density difference (depending on the type of balance and the temperature) the peaks developed a sharp cusp on the front. It is thought that this was due to the sudden onset of turbulent flow through the anemometer. The height of the cusp, once present, rose with increasing density difference [*Figures 6* and *7*).

The results are given in *Tables II* and *III*. The density difference δd was calculated from the percentage of the made-up mixture. Air was taken to contain 20·94 per cent oxygen, 0·93 per cent argon and 0·03 per cent carbon dioxide; mean molecular weight 28·94. Oxygen-free nitrogen was used as a reference gas; this is said to contain approximately 5 p.p.m. of argon. The calculated δd was based on $N_2 = 1$ and was corrected by multiplying by $p/760$ and $273/(273 + t)$ where p was the barometric pressure and t the temperature of operation of the density balance in °C.

The noise of the two balances under various jacket conditions was found to be as follows:

Jacket condition	Skeleton balance μV	Martin balance μV
Air at room temperature	±3·6	±2·3
Circulating water at 11°C	±2·7	
Vapour at 56°C	±2·3	±1·0

Table II. Skeleton Density Balance

Temp. of operation	*Gas other than nitrogen in mixture*	*% v/v of other gas*	*δd (N_2 = 1) corrected*	*μV response (level part of peak)*	*Height of initial cusp over level, μV*
20°C	*Air*	100	0·0305	354	*Nil*
	Air	100	0·0305	356	*Nil*
	Air	4·2	0·0013	14·5	*Nil*
	Air	9·2	0·0028	35	*Nil*
	Air	18·1	0·0055	68	*Nil*
	Air	26·4	0·0080	101	*Nil*
	Air	39·9	0·0122	151	*Nil*
	Air	58·7	0·0179	218	*Nil*
	Carbon dioxide	5·89	0·0318	374	*Nil*
	Carbon dioxide	19·7	0·1049	1110	*Nil*
	Carbon dioxide	26·6	0·140	1328	12
	Carbon dioxide	34·85	0·1835	1612	4
	Carbon dioxide	36·2	0·191	1665	6
	Carbon dioxide	44·4	0·235	1864	30
	Carbon dioxide	53·8	0·282	1937	82
	Carbon dioxide	53·0	0·277	1912	—
	Carbon dioxide	58·9	0·311	2083	168
	Carbon dioxide	67·6	0·358	2155	283
	Carbon dioxide	71·2	0·376	2205	305
	Carbon dioxide	75·5	0·398	2285	355
56°C	*Carbon dioxide*	6·83	0·0322	274	*Nil*
	Carbon dioxide	18·9	0·089	706	*Nil*
	Carbon dioxide	37·0	0·174	1208	*Nil*
	Carbon dioxide	41·0	0·193	1261	25
	Carbon dioxide	47·7	0·224	1405	51
	Carbon dioxide	55·6	0·262	1514	106
	Carbon dioxide	63·0	0·296	1564	163
	Carbon dioxide	70·9	0·334	1605	212
	Argon	100	0·349	1537	139
	Carbon dioxide	80·8	0·380	1652	302

Table III. Martin Solid Block Density Balance

Temp. of operation	*Gas other than nitrogen in mixture*	*% v/v of other gas*	*δd (N_2 = 1) corrected*	*μV response (level part of peak)*	*Height of initial cusp over level, μV*
20°C	*Air*	32·6	0·0103	559	*Nil*
	Air	67·6	0·0213	1139	*Nil*
	Carbon dioxide	5·6	0·029	1432	*Nil*
	Air	100	0·0314	1504	*Nil*
	Carbon dioxide	12·5	0·067	2113	*Nil*
	Carbon dioxide	20·5	0·117	2463	133
	Carbon dioxide	28·4	0·152	2583	369
	Carbon dioxide	35·7	0·187	2616	—
	Carbon dioxide	43·9	0·235	2859	539
56°C	*Air*	32·2	0·0089	383	*Nil*
	Air	67·1	0·0185	719	*Nil*
	Air	100	0·0276	978	*Nil*
	Carbon dioxide	13·1	0·062	1435	*Nil*
	Carbon dioxide	19·9	0·093	1660	77
	Carbon dioxide	27·4	0·129	1788	175
	Carbon dioxide	48·8	0·239	2080	416

Conclusions

(*1*) The skeleton balance is not very much more noisy than the solid model, especially when either vapour-jacketed or with water circulating round it.

(*2*) The response curves of both balances are similar (*Figures 8* and *9*). In this particular case the solid block was approximately three times as sensitive as the skeleton, but this probably depends on the exact location of the thermocouples and the position of the heater.

(*3*) The response of the solid model was approximately linear up to a density difference (N_2 = 1) of about 0·03 (*Figure 8*).

The response of the skeleton model was approximately linear up to a density difference ($N_2 = 1$) of about 0·10 (*Figure 9*).

(*4*) Changing the temperature from 20 to 56°C lowered the response of both models by about 25 per cent (*Figures 8* and *9*).

(*5*) Both models produced a cusp at the beginning of the passage of a sample of gas of δd ($N_2 = 1$) greater than a certain amount. This is thought to be due to the sudden onset of turbulent flow through the anemometer.

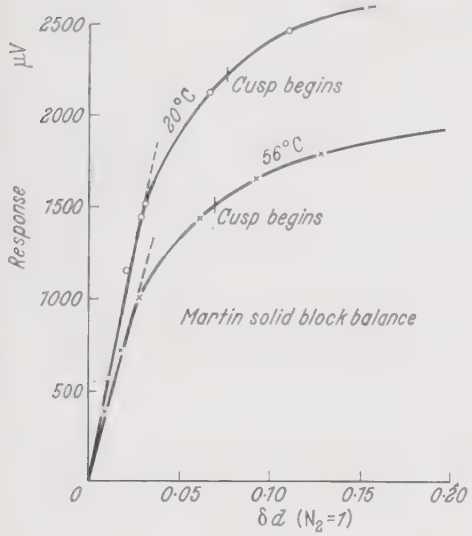

Figure 8. Relation between density difference and electrical response (Martin)

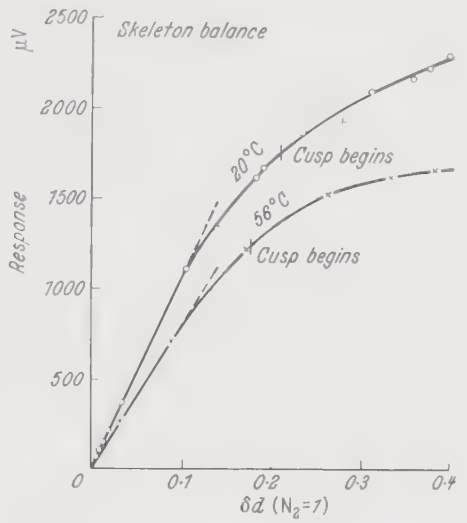

Figure 9. Relation between density difference and electrical response (skeleton)

(*6*) The non-linearity of the balances is probably due to the fact that the anemometer is a low impedance device, and what is theoretically required is a pressure detector of high impedance. In addition the bridge should be a null type in which one of the reference arms is adjusted till the pressure drop across the detector is zero. These conditions are unfortunately difficult to achieve in practice with this type of balance.

Thanks are due to Mr A. J. Clark, who contributed greatly to the experimental work, and to the directors of The Distillers Company Limited for permission to publish this paper.

References

[1] James, A. T. *The Times Science Review*, Summer 1955, p. 8
[2] Golay, M. J. E. *Rev. sci. Instrum.* **18**, 347, 1947

Note: For Discussion see pages 162–168, where Chapters 11–14 are treated together.

14

THE HYDROGEN MICROFLARE DETECTOR USING NITROGEN AS A CARRIER GAS

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The hydrogen flame detector first suggested by Scott has been investigated. Using hydrogen as a carrier gas it was not possible to obtain a straight base line because of the high diffusivity of hydrogen. Therefore nitrogen was used as a carrier, the column effluent being injected into a constant hydrogen stream and burnt at the tip of a capillary. A simple draught shield was provided and the variation in flame temperature was recorded. Constructional and operating details are given.

The response to oxygen, water, oxygenated and chlorinated compounds is compared with the response to hydrocarbons. The accuracy and the reproducibility of quantitative results are exemplified and relative retention volumes for C_4 and C_5 hydrocarbons are given for a diethyleneglycol-monoethylether and for a dimethylformamide stationary phase.

Most workers in the field of gas chromatography have used either a gas density balance or a thermal conductivity cell as detector. Both instruments give excellent results and the thermal conductivity cell can be made so robust that it will stand considerable mishandling by inexperienced operators. However, an instrument mechanic is required to build or repair either detector. At the 1955 Ardeer symposium on gas chromatography, Scott cast an entirely new idea to the audience when he described his microflare detector. The simplicity of construction was bound to appeal to all organic chemists though the protagonists of the more refined instruments previously used were inclined to scepticism. Scott's preliminary results have since been published[1] and there can be little doubt that many laboratories have followed his original suggestion.

Chromatographic Apparatus

The first experiments were carried out using hydrogen as a carrier gas and burning the column effluent at the tip of a glass capillary. The temperature above the flame was measured with a thermocouple and recorded. Whilst the base line was quite steady as long as no sample was in the system, it rose progressively during elution of a sample. The following observations were made:

(*1*) When the sample was introduced, the base line dropped from its previous value

(*2*) Elution of the air introduced with the sample caused a relatively large rise in base line

(*3*) The base line rose in steps as each component of a mixed sample was eluted

(*4*) The rise in base line was most pronounced for peaks which appeared early in the chromatogram.

All these points are illustrated in *Figure 1* which records an analysis of a mixture of C_4 and C_5 hydrocarbons.

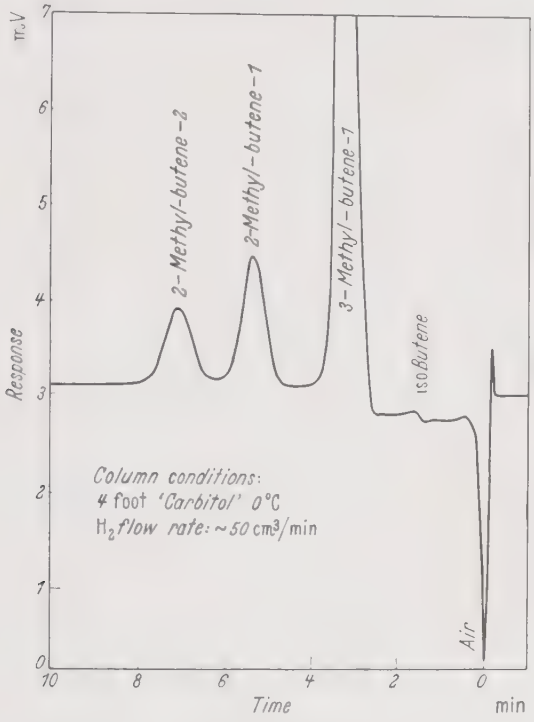

Figure 1. Use of hydrogen as a carrier gas

It was clear that such a chromatogram though qualitatively very useful could not be interpreted quantitatively.

The rise in base line during analysis was not due to any imperfection in the detector and was found to be inherent in the use of hydrogen as a carrier gas. Hydrogen has a very high diffusivity* and the chromatograph column offers little resistance to its passage. The vapours of the sample being analysed, as well as air, have a much lower diffusivity and each chromatographic band therefore acts as a plug in the column. As each component peels off the column the flow rate increases, the flame grows and the base line rises. The increase in flow rate is so marked after the air peak that it is quite apparent with an ordinary capillary flowmeter. Components with a high retention time give a negligible rise in base line since their concentration in the vapour phase is low during their progress through the column.

This base-line difficulty should arise with any flow-sensitive detector such as the thermal conductivity cell if hydrogen is used as a carrier, but this has

* The word diffusivity is not used in its strictly scientific sense since it does not in this case refer to the diffusion of one gas into another but to the ease with which a gas or vapour passes through a column packed with microporous material.

so far not been reported. In order to give results comparable to other detectors, the microflare should be used in conjunction with a carrier gas having a low diffusivity. Two possibilities were considered:

(*a*) the use of carbon monoxide as a carrier gas

(*b*) the use of nitrogen as a carrier gas with an independent hydrogen feed to the flare.

Carbon monoxide would indeed have a low diffusivity as well as a low calorific value and should prove suitable but because of its poisonous nature

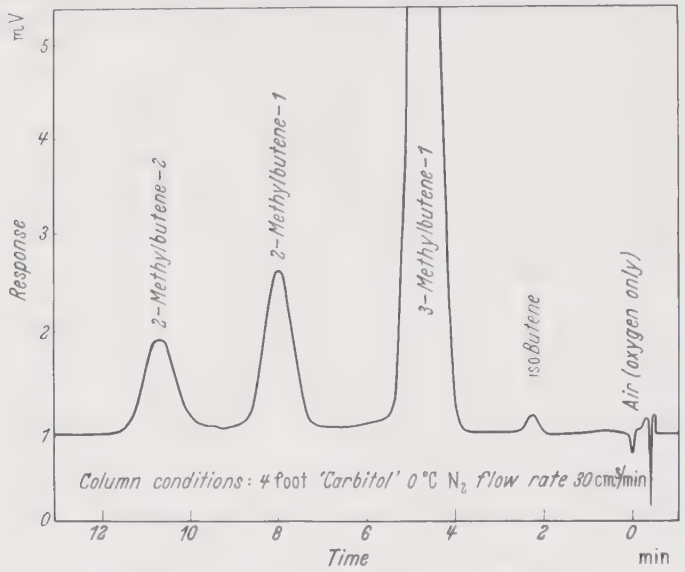

Figure 2. Use of nitrogen as a carrier gas

and the difficult supply position it was decided to choose the second alternative. The results are exemplified in *Figure 2* and appear to confirm the explanation given above.

The system eventually adopted is illustrated diagrammatically in *Figure 3*. Hydrogen from a cylinder is reduced to a constant pressure of 5–10 lb/in.^{2} gauge through diaphragm valves. These are followed by a constant resistance which is merely a 2-foot length of $\frac{1}{4}$-inch copper tube packed with liquid paraffin (40 per cent) on ungraded Celite. The hydrogen is then led directly to the flare. The nitrogen is controlled by a second set of valves and metered through a capillary flowmeter to the head of the column. The chromatograph columns used in the present work were of conventional design, 4 ft or 8 ft long and made from 4-mm internal diameter glass tube. For operation below atmospheric temperature U-tubes were used and maintained at constant temperature in a Dewar flask, rubber connections being used. For operation at or above room temperature a straight tube with ground glass joints was used and the temperature maintained constant with an electrically heated furnace. In this case the capillary leading from the column outlet to the flare must be heated along its entire length by means of a resistance wire wound in series with the furnace.

The flare is illustrated in *Figure 4*. An ordinary tin with a lipped lid forms the shield and the centre of the lid is replaced with 80 mesh copper gauze to allow combustion gases to escape. The thermocouple lead (32-gauge iron–constantan) is clamped to the side of the tin to avoid movement and the

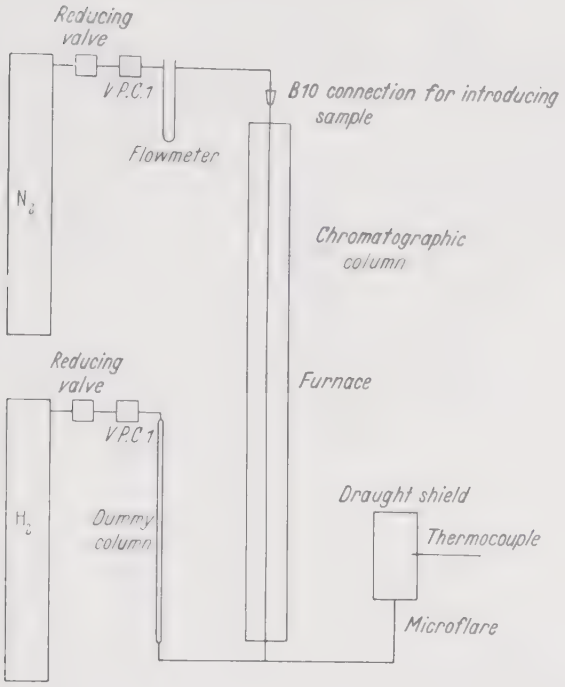

Figure 3. Schematic arrangement of chromatographic apparatus

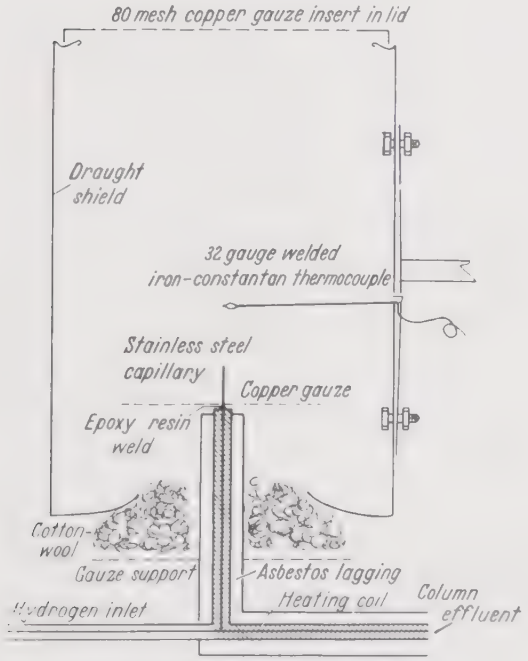

Figure 4. Detector construction

welded tip is placed about 1·5 cm above the flame. The thermocouple lead is not supported inside the tin in order to keep the heat capacity of the system as low as possible. For the same reason the flame burns at the tip of 1·5 cm of 'hypodermic' tube joined with an epoxy resin to the glass capillary. A disc of copper gauze is placed at the foot of the hypodermic in order to break draughts due to convection along the heated portion of the glass capillary. A 5-cm diameter hole is cut in the bottom of the tin and the shield is placed over the capillary, the opening between the lagged capillary and the tin being

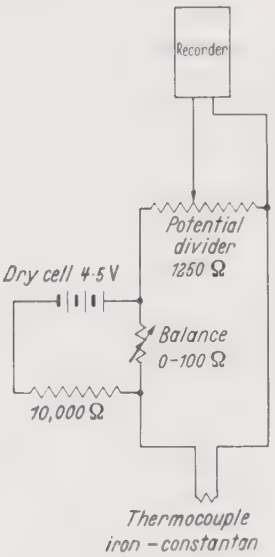

Figure 5. Electrical circuit

packed with cotton-wool to reduce the air supply and eliminate draughts. Though the flare and shield could be constructed in a more rigid form, this has proved unnecessary since it produces a satisfactory base line. The simplicity of construction and the ease with which slight adjustments may be made are qualities well worth preserving.

The electrical circuit is shown in *Figure 5*. The back e.m.f. required to compensate the basic temperature of the hydrogen flame (600–700°C) is provided by a 4·5-V dry-cell battery in conjunction with adjustable decade boxes. The input to the 10-mV recorder is controlled with a potential divider for convenience in adjustment.

Several variables in shield and flare design have been considered and should be discussed. A shield of smaller dimensions reflects back too much heat and requires a long warming-up period whilst a larger shield does not improve its performance. The linear velocity of the draught necessary for combustion should be kept as low as possible and in practice the cotton-wool at the base of the shield regulates this draught. If the flow of air is insufficient, however, water formed by combustion condenses on the sides of the shield and collects in the bottom channel; this has in general been avoided. When the thermocouple is placed 1·5 cm above the tip of the flame, it just glows a dull red when no sample is being burnt. This glow facilitates adjustment. If the thermocouple is placed too low it comes into the cold cone of the flame when a large

peak is emerging: if placed too high the sensitivity is reduced. In early work the thermocouple was silver-soldered but it was found that an inexplicable kink in high peaks was in fact due to the latent heat of fusion of the tiny drop of silver solder used. Thereafter welded thermocouples were used.

When a plain glass capillary was used as a flare it was found that the glass gradually became hotter and hotter and the base line naturally rose at the same time. The hypodermic tip solved this problem and a stainless steel tube of 0·028-inch outside diameter was found to give good results. If this tube is too wide the flame is squat and sensitive to draughts, whilst if it is too fine its resistance to flow forces most of the hydrogen up the chromatograph column when the inlet to the column is opened to introduce a sample.

A hydrogen flow rate of about 100–120 cm^3/min has been used for a nitrogen flow rate of 20–60 cm^3/min. Whilst a lower ratio of hydrogen to nitrogen may be used with a wider bore flare this is not advisable with a hypodermic tip since the flame occasionally blows itself out at low hydrogen concentrations.

The method adopted for introducing the sample on to the column depends to a large extent on the type of detector used. With the gas density balance which is insensitive to flow rate the column inlet is simply opened and the sample introduced with a micro pipette. With a thermal conductivity cell on the other hand it is best to use injection through a serum cap. In the case of the microflare detector using hydrogen as a carrier gas, serum cap injection or a similar technique is desirable to avoid having to light the flame again for each sample. However, with the dual gas stream the detector becomes surprisingly insensitive to nitrogen flow rate and the column inlet may be opened to introduce the sample. In practice when the column inlet is opened some hydrogen flows back through the chromatograph column and the base line is disturbed. This could easily be overcome by having a tap at the outlet of the column. This proved unnecessary as it was found that the base line returned to normal within less than half a minute after the sample had been introduced and the nitrogen supply turned on again. Apart from its simplicity this method of introducing the sample has a certain advantage when operating a column above room temperature. The short time interval between introducing the sample and turning on the nitrogen supply, allows the sample to vaporize before it starts moving through the column. This naturally leads to sharper peaks[2].

Whilst qualitative analysis depends mainly on the nature of the chromatograph column, quantitative analysis depends in the first place on the nature of the response given by the detector. The response of a microflare detector appears to be linear within any one analysis since correct results are obtained when analysing, e.g. 0·5 per cent of benzene in ethylbenzene. Whether response is still linear for very large samples has not been determined but a very small sample requiring an amplification by a factor of 10 on the input to the 10-mV recorder still gives an approximately correct result though the base line is not good enough for great accuracy.

Two factors contribute to the rise in temperature recorded when a sample is burning: (*i*) the flame becomes hotter, and (*ii*) the flame becomes higher. Since the thermocouple is placed well above the visible part of the flame it is believed that the varying height of the flame may be the more important factor.

The sensitivity of the detector is good and the limiting factor is the stability of the base line. It is difficult to define the sensitivity and it is best estimated from *Figure 2* which shows the response obtained with 10 mg of total sample. The largest peak represents a thermocouple output of more than 10 mV equivalent to a temperature rise of approximately 200C°. For a quantitative analysis of well separated peaks a large sample (e.g. 10–15 μl) is used thus taking advantage of a steady base line. For maximum column efficiency in qualitative analysis a very much smaller sample is used (e.g. 1 μl) but the amplified base line instability (± 10 μV at its best) makes quantitative results inaccurate.

Quantitative Results

The reproducibility of results was estimated from a series of eight runs on an accurately weighed mixture of *n*-pentane (containing *iso*pentane as an

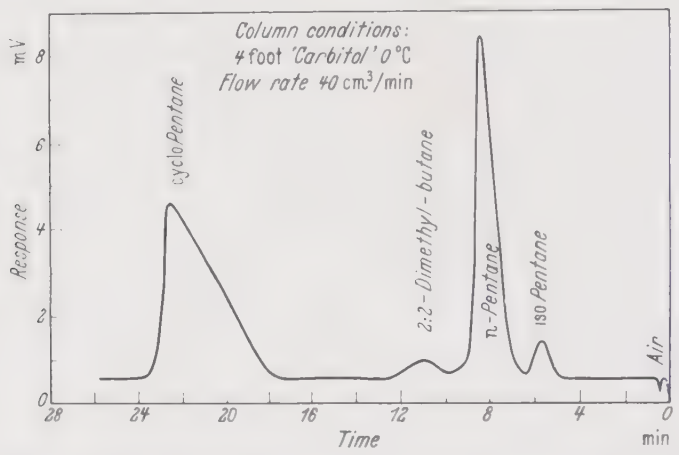

Figure 6. Quantitative analysis of pentane/cyclopentane mixture

impurity) and *cyclo*pentane (containing *neo*hexane as an impurity, see *Table I*). These analyses were carried out on a 4-foot 'Carbitol' column at 0° C with a nitrogen flow rate of 40 cm³/min. A typical chromatogram is shown in *Figure 6*. The marked asymmetry of the *cyclo*pentane peak is due to the size of the sample, it does not affect the accuracy since peaks are still well separated. The results are given below as per cent pentane (including *iso*pentane) on total. The slightly different calorific values of *n*-pentane and *cyclo*pentane were taken into account by multiplication of the area of the *cyclo*pentane peak by a factor of 1·065.

Only one example is given though several mixtures have been tested with similar results. It is believed that the least accurate stage of the analysis is the

Table I. Repeatability and Accuracy of Quantitative Analysis

Per cent *pentane weighed*	1	2	3	4	5	6	7	8	*Average*
43·13	42·9	42·5	43·1	43·2	42·8	43·2	42·9	42·6	42·88

determination of the exact position of the base line. This is partly due to the instability of the detector and partly to the stepping of the recorder (each turn of the slide-wire represents 0·2 per cent of full scale).

For quantitative analysis it was of great importance to determine whether the detector response was in fact proportional to the calorific value of the various components in a mixture. To do this equal weights of two components were mixed and analysed under conditions which would give two fairly close peaks. The column condition and results for some of these mixtures are shown in *Table II*. Most results are in fairly good agreement and it is felt that quantitative analysis may be based on calorific values. Furthermore, this technique may be of some assistance in identifying unknown pure compounds.

Table II. Relative Response of Various Compounds

No.	*A*	*B*	*Response ratio of B to A*	*Ratio of calorific values*
1	cyclo*Pentane*	*Diethylether*	0·79	0·78
2	*Toluene*	*Pyridine*	0·80	0·83
3	*Benzene*	*Methanol*	0·53	0·51
4	*Ethylbenzene*	*Dioxane*	0·65	0·63
5	*Benzene*	iso*Propanol*	0·81	0·76

No.	*Column conditions*	
1	4 foot *Carbitol*	0°C
2	4 foot *Hexaethyleneglycolmonomethylether*	100°C
3	4 foot *Hexaethyleneglycolmonomethylether*	80°C
4	4 foot *Hexaethyleneglycolmonomethylether*	100°C
5	4 foot *Tricresyl phosphate*	50°C

Qualitative Results

Oxygen in the air introduced with the sample appears as a small negative peak and may be seen in *Figures 2* and *6*. The response to oxygen is markedly dependent on the dimensions of the flare tip, a good air peak being obtained with either a wide or a narrow bore but not with an intermediate bore (about 1 mm). Carbon dioxide gives a negative peak following closely on the oxygen peak. Water gives a small indistinct positive peak (preceding *iso*propanol on a tricresyl phosphate column at 120 C). Carbon tetrachloride does not extinguish the flame but gives a small indistinct positive peak. *tert*Butyl chloride, thiophene and similar compounds give a normal response.

Finally, since the choice of various stationary phases is still largely empirical the results obtained with the lower hydrocarbons on polar stationary phases may be mentioned. Whilst a hydrocarbon stationary phase such as hexadecane gives a separation according to boiling points, a separation according to polarizability may be superimposed on this by using a polar stationary phase. This aspect has been discussed by Keulemans[3]. In order to make the

best use of a separation according to polarizability it is desirable to choose a stationary phase with a repeating polar group. If it is too strongly polar, hydrocarbons will have too low retention volumes, therefore a compromise must be sought. Polyethyleneglycols and their ethers have proved suitable for this type of analysis. Diethyleneglycolmonomethylether (Methyl Carbitol) has been used at −40 C to 0 C whilst the monomethylether of hexaethyleneglycol has proved suitable up to 120 C. *Table III* gives the retention volumes relative to *n*-pentane at 0 C. The lengths of the column were 8 feet and 4 feet respectively and the flow rate was 40 cm^3/min but neither of these latter variables affect the relative retention volumes.

Table III. Relative Retention Volumes of Lower Hydrocarbons on Carbitol and Dimethylformamide

Hydrocarbon	*B. pt* °C	*Carbitol*	*Dimethyl-formamide*
Propane	−42·1	0·082	
Propylene	47·7	0·119	
iso*Butane*	11·7	0·190	0·208
n-*Butane*	0·5	0·298	0·374
iso*Butene*	6·9	0·393	0·662
Butene-1	6·3	0·393	0·662
trans*Butene*-2	+0·9	0·512	0·805
cis*Butene*-2	+3·7	0·625	1·0
Butadiene	−4·4	0·738	1·78
iso*Pentane*	+27·9	0·738	0·662
3-*Methylbutene*-1	20·1	0·815	1·15
n-*Pentane*	36·1	1·0	1·0
Pentene-1	30·0	1·28	1·78
2-*Methylbutene*-1	31·1	1·46	2·19
2:2-*Dimethylbutane*	49·7	1·50	1·39
trans*Pentene*-2	36·4	1·61	2·19
cis*Pentene*-2	37·1	1·76	2·42
2-*Methylbutene*-2	38·5	1·93	2·88
cyclo*Pentane*	49·3	2·65	3·16
Isoprene	34·1	2·65	5·55
cyclo*Pentene*	44·2	3·11	5·02
trans*Piperylene*	42·3	3·51	7·69
cis*Piperylene*	44·2	4·02	8·73
cyclo*Pentadiene*	41·0	4·66	11·52

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[3]Keulemans, A. I. M. *Analyt. chim. Acta* **13**, 357, 1955

DISCUSSION

Note: Chapters 11–14 are treated together.

G. R. Primavesi: I should like to make a few additional remarks.

The curves shown in *Figures 8* and *9* (page 153) are extended well beyond the normal density differences encountered in analysis; the highest difference usually

met amounts to about 0·03 which corresponds to about 6 per cent carbon dioxide in nitrogen.

It will be noticed that the skeleton model is linear over about four times the range of the solid but it is approximately one third as sensitive. This is thought to be due to a difference in impedance in the anemometer.

I think the linear range could be doubled by using, as a reference gas, nitrogen containing enough carbon dioxide to give a negative response near the end of the negative linear portion of the curve. This would, of course, be backed off electrically to give a zero. This has not been tried yet.

Recently we have used a 0·003 inch thermocouple pair instead of 0·001 inch in the solid model. This has reduced the response to about one third of its former value but has also reduced the noise which, over 30 minutes, has been as low as $\pm 0{\cdot}05\ \mu V$ with a drift of $\pm 0{\cdot}3\ \mu V$. This improvement is thought to be due to greater rigidity of the thermocouple assembly. At this level of noise the detectable limit (twice the noise level) is given by a density difference of $1{\cdot}6 \times 10^{-5}$ which is about 1 part of amyl alcohol in 100,000 of nitrogen.

It may seem that conclusion (*2*) in the paper is somewhat patronizing, but it is not meant to be so. We think the density balance a very fine device, and have done many hundreds of analyses with it without trouble.

A. J. P. Martin: Both James and I would like to congratulate Primavesi and Munday. It is very nice to see somebody else doing some work on the gas density meter and not merely saying how difficult it is to make, which has been our previous response.

I am puzzled that the authors maintain that only a high-impedance detecting device can give a linear response. I can see no reason why a non-linear response should result from a low-impedance linear anemometer.

G. R. Primavesi: I do not think that is quite correct.

A. J. P. Martin: I would like to go into the matter with you later; I am afraid we cannot argue about it here.

There is one other point too, which I would like to make. You suggested increasing the range of the linear region by unbiasing the bridge to begin with by presumably offsetting the balance rods.

G. R. Primavesi: I did not propose to extend the linear range by altering the adjusting rods, but by using a denser gas in the reference side than that used as carrier gas in the sample side.

A. J. P. Martin: You were not going to do that merely by unbiasing the bridge?

G. R. Primavesi: No.

A. J. P. Martin: Then I withdraw my objection.

J. Haslem: Mr Chairman, I thought I was listening to a new form of analysis this morning because I rather gathered that Mr Scott indicated that his apparatus required no calibration whatever. However, on reflection I think he has really got the advantage that he always knows what is there, and it rather appeared to me, too, that he always has a knowledge of the calorific value of these components.

There is a question I would like to ask him which is concerned with hydrogenation. He said that he had never detected any evidence of hydrogenation in the course of the passage through the tube, etc. I would like to ask him what test he applied as evidence of that hydrogenation.

R. P. W. Scott: Concerning hydrogenation, if you do hydrogenate your sample in the column you will find hydrogenated products evolved from the column. Such products have not been found and quantitative yields obtained definitely indicate, so far, that no hydrogenation takes place.

Secondly, so far as calorific values are concerned, there are values available for all sorts of compounds and I suggest that if you do not know what the sample is you cannot in any case carry out an accurate analysis. One usually wants to know what

substance one is determining; if one does not, a fairly accurate assessment of calorific value can be made provided the type of compound is known.

G. F. Oldham: There is one point I think I could mention which is very useful in identifying unknown substances in chromatograms, and that is to run the mixture through both the hydrogen flame and the density balance detectors, and therefore any given weight percentage of unknown compounds of high molecular weight will give a large response in the hydrogen flame and a smaller response in the density balance, and vice versa. Thus by comparing individual peaks on both types of detector it is then very easy to detect either one, two or three heavy atoms in an organic molecule.

N. H. Ray: May I make a very simple suggestion about the way in which people might record the sensitivity of new detecting devices? It seems to me that in the past it has been customary to record the percentage of full scale deflection on somebody or other's recorder which is produced by some concentration of perhaps a matter of alcohol in nitrogen. Now we are not after all interested in knowing what percentage of full scale deflection can be achieved because clearly you can use any recorder and with a bit of thought you can build an amplifier to give you any magnification you require. What you really should record, I think, is the ratio of some standard signal to the intrinsic noise of the detector, and I would like to suggest that a suitable standard signal can be very easily produced by taking, for example, 1 per cent of air in nitrogen. There is a good reason for choosing air or oxygen as the substance giving the signal because this has an R_F value of unity and so it can be very easily compared from one column to another without regard to the filling of the column. Also, of course, air is very readily available in a pure form.

E. Glueckauf: I should like to refer to some points which were made in Chapter 11 concerning the use of the sonic analyser which is a very sensitive and interesting instrument, but as far as our experience with it goes it requires a fair volume of sample in order to get a sensitive and reliable response. I would like to ask the Chairman whether he could say if, for the purpose of chromatographic analysis, anything has been developed in this way which allows one to analyse such small samples.

A. T. James: I must reply that nothing has been developed. It is to be hoped that someone will develop the necessary apparatus.

A. J. P. Martin: There is one other point I would like to make about the gas density balance, which is that it is quite possible to use it for the estimation of molecular weight of the substances which are coming from the column. This necessitates making two runs with different carrier gases, e.g. hydrogen and carbon dioxide. The response of the density meter is proportional to the density excess of the vapour over the carrier gas and hence comparison of the relative heights of peaks of a known and unknown substance in each carrier gas will give the molecular weight.

I have suggested this on several occasions at my lectures but I never did any experiments on it and I have since heard that Arnoldo Liberti in Italy has quite independently not only thought of it but actually done the work. I am not quite sure when this is to be published but it will appear shortly, and he claims that he can estimate molecular weights to *ca.* 4 per cent.

M. M. Wirth: May I ask you, Mr Chairman, regarding your talk on new forms of detectors, if it is theoretically possible to use the column as its own detector and to measure the heat of vaporization of the sample as it comes off the end of the column?

A. T. James: I have an idea that Mr Phillips made some suggestions about the measurement of heat of vaporization. Perhaps Mr Phillips can reply to that.

C. S. G. Phillips: I am afraid, Mr Chairman, that we have not in fact measured the heat of vaporization. We have, however, measured dielectric constant changes

in a charcoal column, and found this to be quite a satisfactory method of following chromatograms during development.

W. PRIESTLEY, Jr: This last question is a very interesting one. It is exactly the principle we have applied for the last year and a half for detection. The gases or compounds emerge from the top of the column and then pass over a second bed of adsorbent which can be either activated charcoal or any other suitable substance. In our detector activated charcoal is used. As the compounds are re-adsorbed on the activated charcoal you get a temperature rise or fall of the exit gas.

Briefly, the position is as follows. Two detectors are employed. One sees only the reference gas, the other one sees the reference gas plus the separated component. Every few seconds these two streams are switched so that the recorder picks up an oscillating signal. This signal can be integrated, so here is a detector that can give you not only peak heights but also mass response. This has now been extended to the point where these two detectors are completely eliminated. The flow of a given component through the end of the column is sensed by inserting a thermocouple directly into the end of the column. As the component goes by, the thermocouple temperature rises and acts as a very sensitive detector; the signal is proportional to the amount of the component.

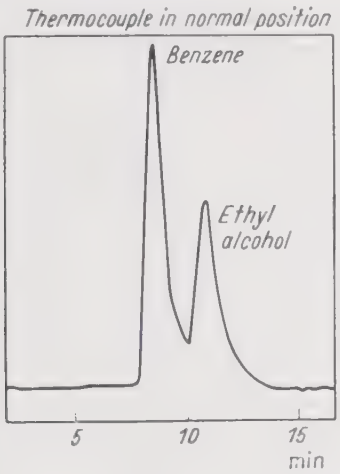

Figure 3.1

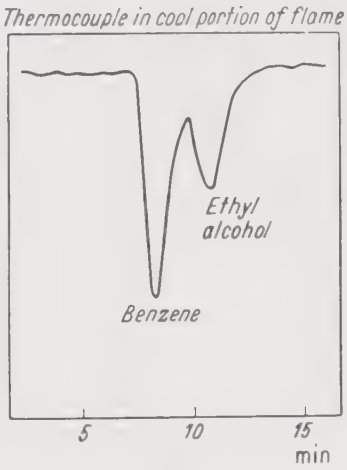

Figure 3.2

Column details: PEG 600 (20% w.w.) *on* 44/85 mesh *brick*. 130 cm × 0·3 cm. 78°C
Carrier: nitrogen, 30 ml/min. *Flow to jet: hydrogen*, 25 ml/min

C. G. SCOTT: Our work carried out with a simple combustion detector of the type described by R. P. W. Scott (see *Figure 1*, page 132) has given orders of stability and sensitivity similar to those quoted in his paper. We did find, however, with our apparatus that the sensitivity was at its best when the amounts of hydrogen fed to the burner were kept at a minimum. This was accomplished at first by using either 75/25, 50/50 or 25/75 hydrogen mixtures as the carrier gas. This was later changed to a system similar to that reported in Dr Wirth's paper. With the latter system he found that a hydrogen flow rate of 25–30 ml/min was sufficient to give trouble-free operation for nitrogen flows ranging from 10–75 ml/min. Comparing Dr Wirth's results with those obtained by R. P. W. Scott, I find them poorer with regard to both stability and sensitivity. I think that this poor stability and sensitivity can be attributed to two related factors: (*1*) the very high hydrogen flow rate used—namely 100–120 ml/min—and (*2*) the lack of any real attempt at insulation and exclusion of draughts which, apart from causing instability, is also a reason why high hydrogen flow rates have to be used in order to maintain the flame.

One further point is that Dr Wirth states that of the two factors contributing to the rise in temperature of the thermocouple the increase in height of the flame may be the more important factor. I would like to give some results to suggest that it is in fact the only factor, see *Figures 3.1* and *3.2*. Using an approximate 50/50 blend of benzene and ethyl alcohol run on a PEG 600 column with the jet and couple in their normal position for quantitative work, two peaks are obtained, the smaller peak for the ethyl alcohol being due to its lower heat of combustion. With the conditions under which our detector is run, it is possible to locate the thermocouple in the cool part of the flame so that it cools as the flame rises during combustion, resulting in a series of inverse peaks.

The inverse peaks for the benzene–alcohol blend are similar to those run under normal conditions. I think, then, it is reasonable to assume that it is unlikely that the heat due to the combustion of the sample takes any part in the actual cooling of the thermocouple, and it is suggested therefore that the only factor contributing to the temperature rise even in the normal operating position is the increase in height of the flame, which for some reason is proportional to the heat of the combustion.

G. F. HARRISON: We have done a small amount of work using the Scott combustion detector, but we have not been able to develop it to the extent which the device merits. I feel that it is a most promising form of detector and it is one we are going to pursue with alacrity as soon as possible, but there are one or two minor points to which I would like to draw your attention when using hydrogen as a carrier gas.

We started with this device on the column which I described in my paper, which we used for the analysis of methane–ethylene gas streams, and we found that with that apparatus it was quite impossible to determine the methane with the flame detector, the reason being that there is a very great disturbance of flow as soon as the sample is put on the column. Immediately there is a drastic drop in zero, followed by a fairly quick recovery. Methane comes through very quickly and is in fact emerging from the column before the zero is stabilized. With a small amount of methane the effect is not seen; with a larger amount the disturbance is such that it is quite impossible to use the method for quantitative analytical purposes. This experience rather put us off this particular detector, but in collaboration with C. Scott we managed to find the answer to this rather annoying phenomenon, and that is to use a mixed carrier gas, e.g. a nitrogen–hydrogen mixture or to use pure hydrogen and burn it outside, when you get very little disturbance in injecting the sample. We assumed that this sudden depression was due to the blocking of the column by dense gas—a solid flow of dense gas in the column restricts the flow of hydrogen so that the flame shortens. Dr Wirth told me that hydrogen had greater viscosity than methane–ethylene, so that this explanation may not be true.

I think one reason why R. P. W. Scott never had trouble of this type was that he was using very much smaller sample volumes than we did and because his detector is very much more sensitive than a normal katharometer. We were trying out this apparatus in series with a katharometer. For this reason we used sample volumes of the order of 3 mm^3, which is relatively a large sample volume for the flame detector.

Also Mr Scott tells me he has not done much work on gas samples, most of his results being obtained with liquid samples. I do not think you get plugging of the column to quite the same extent with the latter.

H. BOER: First I would like to comment on Chapter 12. I would like to express my sincere appreciation of R. P. W. Scott's development of this remarkably simple detector. I think that it will contribute greatly to the widespread application of GLPC or GLC, though it can only be used if the components are not to be recovered. My questions arise merely from the thought that the value of the instrument would

be enhanced if its quantitative response could be improved. I feel that its great susceptibility to flow variations is the main source of difficulty. Perhaps the author can tell us something more about this point.

Secondly, the base line instability has to be considered. On page 134, 'Characteristics of the detector', you adjust the sensitivity so that a zero instability of less than 1 per cent is obtained. I should like to know the character of this instability: short term (noise), fluctuations or drift. From *Figure 3* (page 133) one would conclude that this drift is more than 1 per cent, which would be rather serious for an integrator coupled to a recorder.

On page 135, section 2, the measurement of peak height involves the mean of two minima and the stated difference between these two minima suggests that even at 1/20th of maximum sensitivity base line stability is rather poor. Is it possible that part of this instability is caused by the rather sensitive recorder? In that case it would be better to use a recorder of, say, $2\frac{1}{2}$ mV and a higher sensitivity setting of the detector.

In the Chapters 14 and 28 some attention is given to the phenomenon of bands 'plugging' the chromatograph, resulting in base line fluctuations. According to Harrison, the use of a mixed carrier gas 'largely eliminates' this effect. It might be that this effect still influences the base line and thus the accuracy of the analysis.

According to Wirth, a brazed thermocouple junction gave rise to a kink in high peaks due to the heat of fusion of the solder used. Was this phenomenon not observed, or is the melting point of the brazing alloy sufficiently high to prevent melting?

I have only a few points on Chapter 14. The modification of Scott's detector, which is described here, is attractive in that it enables a single gas to be used as carrier instead of a mixture. Furthermore, the construction can hardly be simpler. On the other hand, as far as I can gather from the paper, the useful sensitivity seems to be somewhat affected by this simplification and perhaps by the fact that the flow instabilities of two gas streams both exert a certain influence, resulting in a decreased base line stability.

It is not quite clear to me what is meant by the statement that 'correct results are obtained when analysing 0·5 per cent of benzene in ethylbenzene'. Are these values related to exactly known amounts of sample, or is an internal standard used?

On page 160 an 'amplified base line instability of ± 10 μV at its best' is mentioned. On a 10 mV recorder this would be ±0·1 per cent of full scale, which I think is not too bad and which should not seriously interfere with quantitative analysis. Probably the base line instability as such is meant, without amplification.

R. P. W. Scott: Concerning Dr Boer's comments, first I must admit the detector is sensitive to flow changes, but we have satisfactorily arranged the flow to be sufficiently constant not to cause any serious trouble. I was interested in this possibility of the recorder noise, as opposed to detector noise, causing instability. The instability that I have stated as 1 per cent includes—it is very difficult to assess this—probably 0·75 per cent drift on which is superimposed probably 0·25–0·5 per cent of actual zero noise; but I have never measured it, it is just my general impression.

The measurement involving base level as the mean of the two minima was included because I wanted to impress that the zero stability which I stated was continuous on either side of the peak, and to eliminate any idea of this stepping effect which is reported for this detector.

Improvement of quantitative results: you suggest that gas flow might influence quantitative response. I assume that you infer that the inaccuracies are due to zero instability, but I do not think so. I think the only inaccuracy of the order I am getting in quantitative results (1 per cent) is due to the fact that the linear response of the whole detector does fall off a little when you get to very high peaks. In other

words, very high peaks are not measuring the true height—there is a slight lag. That may be thermal in the detector itself; it might be the actual response of the thermocouple not being sufficiently linear at the rate at which it is working.

There is one point about Mr Scott's note about the inversion of peaks. I think that is largely due to the fact that he is using a very small quantity of hydrogen relative to nitrogen and the actual flame area is large—you have got a very large zone in the centre which is not anywhere near the external part of the flame that still further accentuates this effect of flame length. If you use 75 per cent hydrogen and 25 per cent nitrogen you cannot detect peak inversion.

M. M. WIRTH: Two or three questions have been asked; one concerning the thermocouple. The low-melting brazing alloy has now been replaced by one melting at about 1000 C. With lower-melting alloys, i.e. with m. pt 600–800 C, the peak shape is distorted.

I think it is an advantage to have a simple apparatus because it is easy to set up any number of detectors and have any column ready for use immediately—all that may be necessary is to turn the nitrogen supply from one column to another—and fix a selector switch for the correct thermocouple.

Stability of base line: you can argue incessantly about the stability of the base line. My only requirement is to see the actual chromatograms, which is why I passed them round so that you could judge their zero stability for yourselves. When I mentioned the 0·5 per cent benzene, this was a sample analysed which had been made up by others specially for the purpose and we did not know the concentration of benzene. What I am implying is that the response for very small peaks gives the same quantitative results as the response in large peaks.

Base line amplification: I talked about ± 10 μV. We determine this by amplifying the output of the thermocouple with an amplifier which is not at all suitable. The amplification was increased until we have a definite variation in the base line by which we estimate the zero stability. On good chromatograms the base line stability is of the order of 0·1 per cent. The main cause of movement or inaccuracy in the base line is 'stepping' on the recorder; while the recorder gives a very good smooth base line on large rapid peaks, when you come down on the tail of a peak the recorder steps very badly and occasionally this remains on a certain level for as long as a minute before it steps down to the correct level. These steps are rarely more than 0·3 per cent of full scale, but on the base of a large peak this can make quite an important difference in quantitative analysis.

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A COMPARISON OF DETECTION METHODS FOR GAS CHROMATOGRAPHY INCLUDING DETECTION BY BETA RAY IONIZATION

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An account is given of the requirements that a method of detection for gas chromatography should fulfil, and several of the available detecting systems are compared. It is concluded that the methods employing the thermal conductivity cell and ionization by β-rays from a radioactive source at present appear to be particularly versatile and suitable for purposes of general routine analysis.

The method involving β-ray ionization is described in some detail.

An extremely important part of the apparatus required for gas–liquid and gas–solid chromatography is the equipment for sensing and recording the presence of components in the effluent gas. One of the objects of the present paper is to compare the suitability of various proposed systems of detection.

It is convenient to divide the detecting methods employed into two types: (*i*) the differential, and (*ii*) the integral, type. They may be defined as follows:

(*i*) A differential sensing device essentially responds to and indicates some momentary property of the effluent gas. In elution gas chromatography, which gives bands of components separated by bands of pure carrier gas, it produces a chart showing a base line (corresponding to the property in question of the carrier gas), on which peaks for the components are superimposed.

(*ii*) The integral type of detector records the integrated value of some property of the effluent gas and thus gives a chart showing a number of ascending steps.

Though any form of differential detection could conceivably be converted into integral detection by some electronic or mechanical arrangement, the second type has only been employed in practice for systems involving titration and pressure measurements in a vessel, where the value determined itself constitutes a summation. Most of the delicate systems of detection proposed for separations involving small concentrations are of the differential type, and only this class will be considered here.

In theory a system of detection for the purpose in view could be founded on any of the following three basic principles: (*a*) on a change in gas flow rate due to the emergence of the component, (*b*) on the reduction in concentration

of the carrier gas, and (*c*) on a change in some property determined by the presence of a certain concentration of a component. Whilst methods (*a*) and (*b*) have the attractive features of eliminating the need for calibration, no systems based on these principles are as yet available, mainly owing to the fact that they involve accurate measurements of small changes in large values. It is possible that such methods may become available in future. All methods of detection to be discussed at present are based on principle (*c*).

Requirements for Detecting Systems

(*1*). The main property that a detecting device for gas chromatography should possess is a *high sensitivity* to the presence of a component in the carrier gas. This requirement is dictated by the fact that the efficiency of separation in the column increases with the decrease in the size of the sample analysed. However, the magnitude of the signal (which is easily amplified) is not the only requirement. It is equally essential that the base line shall be stable and not be subject to slow variations ('drift') or to rapid fluctuations ('noise'). These phenomena, which together may be designated as the 'base line instability', if excessive, largely detract from the significance of a high overall sensitivity.

It is obviously desirable to have a satisfactory basis for comparing the overall sensitivity of various methods of detection. Dimbat, Porter and Stross[1] propose calculating it by the formula

$$S = A \,.\, C_1 \,.\, C_2 \,.\, C_3/W$$

in which S = sensitivity in cm^3 mV/mg; A = peak area on chart in cm^2; C_1 = reciprocal chart speed of recorder in min/cm; C_2 = recorder scale in mV/cm; C_3 = flow rate of carrier gas at column outlet, corrected to measuring cell conditions, in cm^3/min; W = weight of component in mg. In addition to S, the base line instability should be stated in millivolts.

The sensitivity as defined above refers to the peak area found for a given weight of component, i.e. to the total aggregate of column and detector. For investigating only the sensitivity of the detector and its reaction to various influences it is convenient to employ a simple flow method, in which a standard mixture of a carrier gas and a certain component is passed through the detector. In the laboratories with which the writer is connected it has become the general practice to employ for this purpose carrier gas that has been saturated with pure *iso*octane (2:2:4-trimethylpentane) at 0° C.

Other desiderata, besides a high useful sensitivity to the components, will only be briefly mentioned. They include:

(*2*). Rapid response.

(*3*). Proportionality between the signal and the concentration of the component ('linearity').

(*4*). Constancy or predictability of the response for various types of components, with a view to facilitating or eliminating the need for calibration.

(*5*). 'Versatility', or adaptability to a wide range of circumstances. The method should, for instance, preferably be suitable for use at high temperatures, since there now exists a strong tendency to extend gas chromatography to less volatile compounds. The detecting system should not exclude certain classes of components (e.g. halogen compounds, etc.).

(6). Low susceptibility to fluctuations in rate of gas flow, pressure and temperature.

Some further points of a practical nature are: ease of construction, low cost, robustness and simplicity of the auxiliary equipment.

Available Differential Detecting Methods

Of the differential methods of detection that have been employed, the following will be mentioned:

1—Detection by thermal conductivity. This widely used method, first employed in chromatography by Claesson[2], will be referred to later.

2—Detection by gas flow impedance (Griffiths, James and Phillips[3]), in which the pressure differential set up by the gas flowing over an orifice or capillary is measured.

3—Detection by surface potential (Griffiths, James and Phillips[3]), based on a measurement of the e.m.f. set up over a vibrating condenser formed by two plates, one of which is preferably coated, for instance, with a fatty acid or collodion.

4—Detection of organic compounds in the form of carbon dioxide after combustion over copper oxide (Martin and Smart[4]). The properties of this system will depend upon the device used for recording the carbon dioxide (infra-red analysis, thermal conductivity, etc.). Complete combustion is obviously essential.

5—Detection by density differences of the effluent and the carrier gas. A highly sensitive instrument, the 'gas density balance', was devised for this purpose by Martin[5].

6—A detection method that involves using hydrogen as carrier gas, burning this gas in a jet placed below a thermocouple and measuring the variations in temperature of the latter[6].

7—Detection depending on the ionization of the gas caused by exposing it to radiation and measuring the current passing between two electrodes over which a d.c. potential is maintained. A method of this nature, employing β-rays from a radioactive source for ionization, will be described in this paper.

(Various other systems of detection—e.g. by the dielectric constant and the velocity of sound—have been proposed, but will not be considered here owing to lack of information.)

Experience in the laboratories with which the writer is associated has been mainly limited to methods 1 and 7, though some tentative experiments have been done with systems 2 and 4. Nevertheless an attempt has been made to draw up a table showing, in very rough qualitative terms, the suitability of the various systems of detection for general routine analyses (*Table 1*).

The evaluations given for individual aspects of the systems are admittedly open to discussion. They were assigned—where experience was not available—from the information published in the literature (if any), from a consideration of general physical principles and from information gained in discussions with other investigators.

By assessing the various properties of the methods of detection in such a manner, the conclusion has been reached in the author's laboratory that thermal conductivity and β-ray ionization at present appear to be the two systems most attractive for development, particularly with a view to their

Table I. Tentative Comparison of some Differential Detection Techniques
+ favourable — unfavourable

	Sensitivity, including background stability	*Linearity and calibration*	*Response time*	*Auxiliary equipment ease of construction, maintenance*	*General applicability*	*General remarks*
β-ray ionization	+	+	+ +	+	+	*Adaptable to high temperatures (250°C or above)*
Thermal conductivity	+	−*	+	+ +	+	*Limited range of temperature*
Gas density balance	+ +	+	+	−	+	
Hydrogen flame	+	+	+	+ +	−	*Halogenated compounds may extinguish flame*
Total combustion + infra-red	+ +	+	− −		−	*Complete combustion difficult: probably limited to hydrocarbons and oxygenated compounds*
Total combustion + other diff. det.	+	+			−	*do.*
Gas flow impedance	−			+		
Surface potential		− −	− −		−	*Highly sensitive in specific cases only*

* More favourable with hydrogen or helium than with nitrogen as carrier gas (cf. ref. 1)

suitability for a wide range of applications in routine laboratories. Some features of these two detectors will therefore be considered here, and a description of the β-ray method will be given.

The Thermal Conductivity Cell

Thermal conductivity cells are well known and are to be discussed in a paper by A. J. Davies and J. K. Johnson and in communications by several other investigators at this meeting. Some general considerations on its features may, however, be given here.

As the instrument is generally used without d.c. amplification beyond that provided by the recorder, a high voltage output from its bridge is desirable. This can be attained by using long, thin heater wires. Cells with thin tungsten

spirals may be constructed and are available commercially. Such instruments can attain a sensitivity, as defined previously, of $S = 300$ cm³ mV/mg with a 'noise level' of 0·005 mV (helium as the carrier gas)[1]. Experience has shown, however, that katharometers with coiled heaters must be designed with extreme care if a severe base line drift is to be avoided. For this reason the cells at present used as standard in the Koninklijke/Shell-Laboratorium, Amsterdam, employ 20-μ straight platinum heater wires maintained under tension by springs*. ($S = 12$ cm³ mV/mg for toluene with nitrogen as the carrier gas.)

All thermal conductivity cells nevertheless require a very close regulation of heater current, whilst even the best instrument may show a certain unbalance by an equal variation of wire temperature, wall temperature and gas flow rate in the two channels simultaneously. The katharometer is sensitive to variations in gas flow and pressure, but the latter factors may be largely overcome by a proper connection of the channels in the gas flow system.

A definite drawback of detection by thermal conductivity is the large amount of calibration required; moreover, calibration data only hold for a particular set of operating conditions†.

As stated previously, the use of a detector at higher temperatures is now becoming more and more important. As the wire temperature may be as much as 100C° above the temperature of the katharometer walls, phenomena of carbon deposition on the hot wires will be the principal factor limiting its operability at such temperatures. In this connection it may be remarked that cells have occasionally been used at 225°C wall temperature without trouble; in other cases, operation even at 200°C has given rise to difficulties. Carbon deposition shows up as an increase in the base line instability. It is therefore felt that the useful operating temperature of this detector as a rule will have an upper limit of approximately 225–250°C. Furthermore, with nitrogen as reference gas a higher katharometer temperature results in a decrease in sensitivity.

Detection by Beta Ray Ionization

Measurements of the current passing between two electrodes at different potentials in a gas ionized by some form of radiation have been used for analytical purposes by various investigators. A method based on this principle, employing β-rays emitted from a radioactive source and a convenient form of apparatus[7], was developed for gas analysis in the Emeryville (Cal.) laboratory of Shell Development Company, and essentially the same procedure was applied there for detection in gas chromatography[8]. The latter aspect has also been investigated in the writer's laboratory.

The method can be outlined with the aid of the diagram given in *Figure 1*, which represents the apparatus used by the writer. As in several of the preceding methods, a differential system is adopted, employing two cells, one for the carrier gas and one for the column effluent. If the outlets of the two

* When using the same cell design with 5-μ diameter tungsten wires and hydrogen as the carrier gas a sensitivity value $S = 600$ cm³ mV/mg is obtained, with a noise level of 0·0125 mV.

† See footnote to *Table I*.

cells are coupled as shown, pressure and temperature variations in the two compartments will be identical and their effect is largely eliminated.

The gas in the cells is bombarded with β-rays from a radioactive source. The cells have a common central electrode; separate sources of stabilized voltage are connected between the walls of the cell and the central electrode.

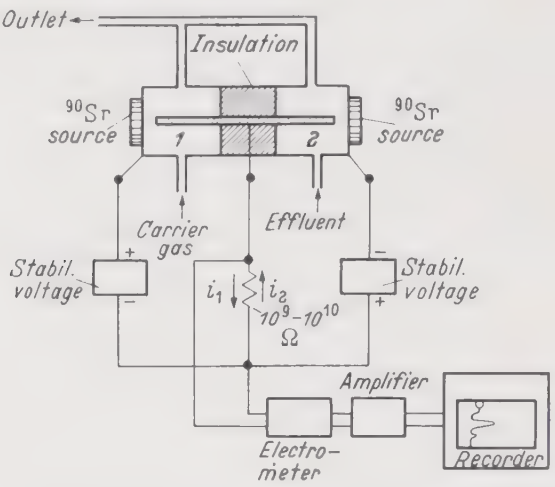

Figure 1. Circuit diagram of β-ray detector
1,2. Ionization chambers

The two ionization currents, which are arranged to be opposed, pass through a common high resistance (10^9–10^{10} ohms). Any voltage developed across the latter owing to current variations, which are of the order of 10^{-11} A, is transferred to an electrometer–amplifier (impedance converter), and thence to the recorder*. The source of radiation that has been utilized is radioactive strontium (^{90}Sr); this is commercially available in needle or button form for medical purposes and only produces β-radiation, the fission reaction being

$$\underset{\text{half-life } ca.\ 25\text{ y}}{^{90}\text{Sr}} \xrightarrow[0{\cdot}6\ \text{MeV}]{\varepsilon} \underset{\text{half-life } ca.\ 60\text{ h}}{^{90}\text{Y}} \xrightarrow[2{\cdot}5\ \text{MeV}]{\varepsilon} \underset{\text{Stable}}{^{90}\text{Zr}}$$

In anticipation of the later description, the advantages of this system of detection may be summed up as follows:

1. It is extremely sensitive
2. Calibration is virtually unnecessary, since the differential ionization currents may be predicted from the ionization cross sections of the component molecules
3. The cell itself is very simple to construct
4. It is adaptable for use at high temperatures
5. It is inherently insensitive to changes in gas rate.

* Shell Development Co. workers[8] have developed a slightly different form of apparatus for gas chromatography; they employ a single ionizing chamber and balance the ionization current electrically.

Disadvantages are:

1. The auxiliary apparatus required is more elaborate and costly than for the thermal conductivity method
2. Precautions are necessary in handling the radioactive source.

^{90}Sr in its container or in the apparatus is virtually harmless, since the β-rays (the only form of radiation) are entirely shielded off, and the same

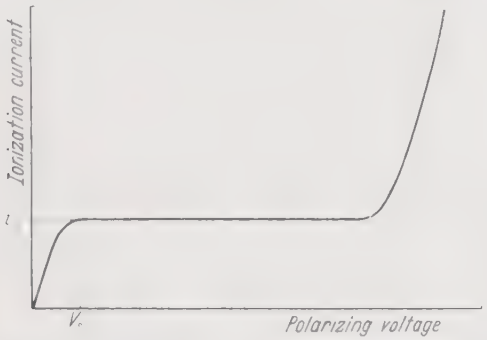

Figure 2. General shape of ionization current curve

largely applies to the x-rays formed by impact of electrons with the walls. By its analogy to calcium, however, ^{90}Sr is readily taken up by the body and, in view of its long half-life, thus forms a source of potential danger. If proper care is taken not to damage or disturb the radioactive source, this danger can be largely avoided.

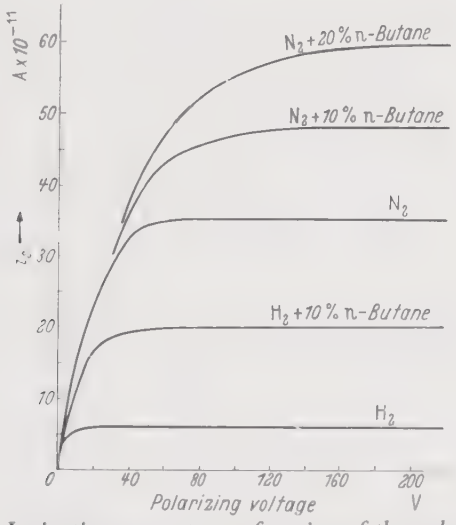

Figure 3. Ionization current as a function of the polarizing voltage

Some aspects of this system will now be considered in detail.

The current passing through the ionized gas between the electrodes depends upon a number of parameters.

At a certain intensity of bombardment and with a certain type of gas, the current varies with the polarizing voltage, as shown diagrammatically in *Figure 2*. Below a certain voltage V_s the ionization current i_s increases with the potential applied. In a considerable voltage range above V_s the current

remains constant; it is then termed the saturation current. At much higher potentials, secondary ions are emitted by impact, and the current rises steeply.

As can be seen from *Figure 3*, the value of V_s depends on the kind of gas present; it tends to higher values as the average ionization cross section of the molecules increases.

V_s also depends upon the geometry of the ionization chamber; in general, polarizing voltages of 85–100 V may be used if hydrogen is the carrier gas and the sample concentration is low; with nitrogen and/or larger concentrations of components, stabilized potentials up to about 300 V may be required.

With increasing intensity of radiation more ions are formed and i_s increases. At the same time the fluctuations in i_s, which are a result of the statistical fluctuations in the emission rate, relatively decrease, as the relative standard deviation of the total emission rate is inversely proportional to the square root of this parameter. This results in an increased signal-to-noise ratio with stronger radiation sources. The 25-mc ^{90}Sr sources now in use emit some 9×10^8 electrons per second, probably one third of which passes into the chamber. This chamber, under average conditions, contains about 5×10^{19} molecules. Even if we assume that every electron produces more than one ion pair, the number of ions formed is only a very small fraction of the total number of molecules. This again indicates a possible gain in sensitivity by increasing the strength of the source. On the other hand, when all molecules are ionized, the composition of the gas no longer plays a part, except in so far as manifold ionization occurs. It is hence to be expected that there is an optimum strength of source for a certain set of chamber dimensions.

Since the value of i_s with nitrogen is higher by a factor of about 5 than with hydrogen, the statistical variations in the β-rays will have a larger influence on the current in the former case; the base line stability will therefore be better for hydrogen than for nitrogen.

Owing to the very low time constant (*ca.* 1/1000 sec) of the ionization and electrical transport phenomena, the detector should be essentially insensitive to flow, and the response time of the instrument only dependent on the volume of the chamber. The insensitivity to flow has been confirmed for variations in gas rate as high as 8 : 1. At very high gas rates constrictions in the outlet ports of the chambers may give rise to pressure effects.

Experiments (employing a 5-mc source of 2 cm^2 radiating area and 10 per cent butane in nitrogen or hydrogen) further showed that there exists a certain optimum for the depth of the chamber. Under the above-mentioned conditions this was found to be 14 mm. Surprisingly, this value is only a fraction of the length of the free path of high energy β-rays (e.g. in air), which amounts to several metres.

Since i_s depends on the number of ions formed, and thus on the number of molecules present, it is sensitive to variations in both temperature and pressure. By using the twin-cell arrangement and connecting the two cells as shown in *Figure 4*, the influence of these variations can be made very small, even when temperature and pressure control is but moderately good.

If we assume ionization to be additive, the signal of the compensated cell may be expressed as

$$s = mi_s^c + (1 - m)i_s^g - i_s^g = m(i_s^c - i_s^g)$$

where s = signal, m = molar fraction of component c in carrier gas g, i_c^c, i_g^g = saturation current of the pure component or carrier gas respectively in the chamber under consideration.

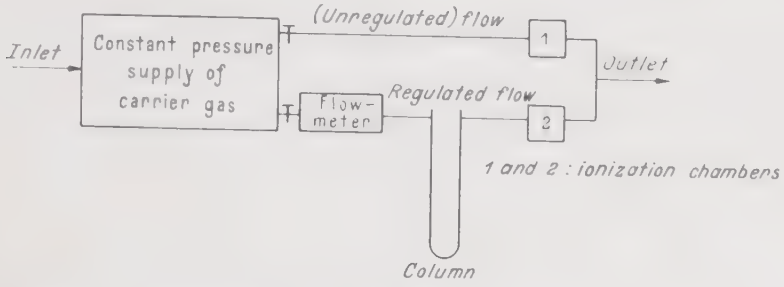

Figure 4. Arrangement of gas flow through chambers of β-ray detector

From this formula it follows that the response of the β-ray detector should be linear with respect to concentration, a fact that has been confirmed in several cases. Furthermore, when i^g is much smaller than i^c (as is generally so) the magnitude of the signal will be largely independent of the type of carrier gas, contrary to what is observed when using thermal conductivity.

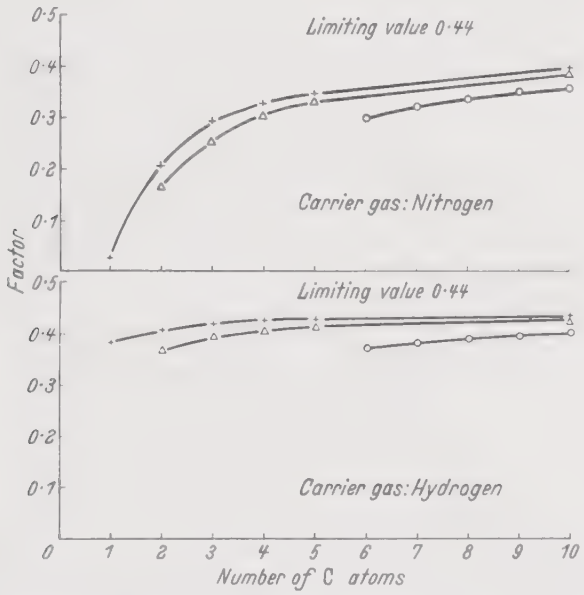

Figure 5. Calculated calibration factors for various classes of hydrocarbons
Paraffins △ *Olefins and monocyclic naphthenes* o *Mono-aromatics*

The value of i_c is directly related to the ionization cross section Q of the molecule: the magnitude of this parameter should hence be known for each component. It has been found[9] (at all events for hydrocarbons) that the value of Q for a molecule can be calculated with fair accuracy by adding the values for the component atoms. Thus for a hydrocarbon C_nH_{2n+p} we have

$$Q_{\text{hydrocarbon}} = nQ_{\text{carbon}} + (2n + p)Q_{\text{hydrogen}}$$

in which $Q_{carbon} = 4{\cdot}16$ and $Q_{hydrogen} = 1{\cdot}00$. As Q is a molecular parameter, the calculation should be independent of chamber geometry, temperature and pressure, as long as constant conditions have been maintained throughout the analysis. In the graphs shown in *Figure 5*, the proportionality factors for converting weight of component to peak area have been plotted for the members of a number of hydrocarbon types. In each case this factor is found by the formula

$$\text{Factor} = \frac{Q_{component} - Q_{carrier\ gas}}{\text{Mol. weight of component}}$$

(For nitrogen as carrier gas $Q_{nitrogen} = 3{\cdot}84$.)

In interpreting a chromatogram, the measured peak area of each component is divided by its appropriate factor; the quotients thus obtained for all peaks are added; the percentage by weight of each component is found by calculating the percentage of its quotient on the total.

The agreement found by this procedure with known percentages may be illustrated by the following example found in an analysis of a synthetic hydrocarbon mixture.

Table II. Percentages found by Beta Ray Detection on the Basis of Theory for the Components of a Synthetic Hydrocarbon Mixture

Component	*Value calculated from peak area* per cent	*Actual percentage by weight*
1 *Benzene*	16·3	16·5
2 *Toluene*	17·2	17·0
3 *Ethylbenzene*	17·0	17·1
4 *Cumene*	16·2	16·2
5 t-*Butylbenzene*	17·2	17·4
6 p-*Cymene*	16·1	15·7
5 + 6 (*slight overlap*)	33·3	33·1

The validity of this procedure for compounds other than hydrocarbons and for very diverse concentrations is still being investigated.

The sensitivity of the β-ray detector, employing 25-mc ^{90}Sr sources, is high and is at least equal to that of the maximum reported for the thermal conductivity cell (viz. that obtainable with tungsten wires and hydrogen). Under average conditions the detectable amount of substance is about one microgramme. The value of S for the toluene peak of *Figure 8* amounts to 600. As follows from *Figure 5*, sensitivity is somewhat lower at low molecular weights.

The noise level with 25-mc sources amounts to approximately 0·5 per cent of full scale deflection (0·0125 mV on a 2·5-mV recorder), so that it is about the same as that of the most sensitive type of katharometer and slightly less than that reported for the gas density balance. 'Noise' is, however, somewhat more apparent on the β-ray charts, as it has a shorter period than in the two other cases.

The writer believes that any electrometer–amplifier of sound design may be employed as impedance converter, provided it is run continuously to avoid

excessive drift. Most of the author's experiments have been done with a commercial vibrating reed instrument, but his American colleagues have employed a d.c. electrometer-amplifier. A condenser should be connected

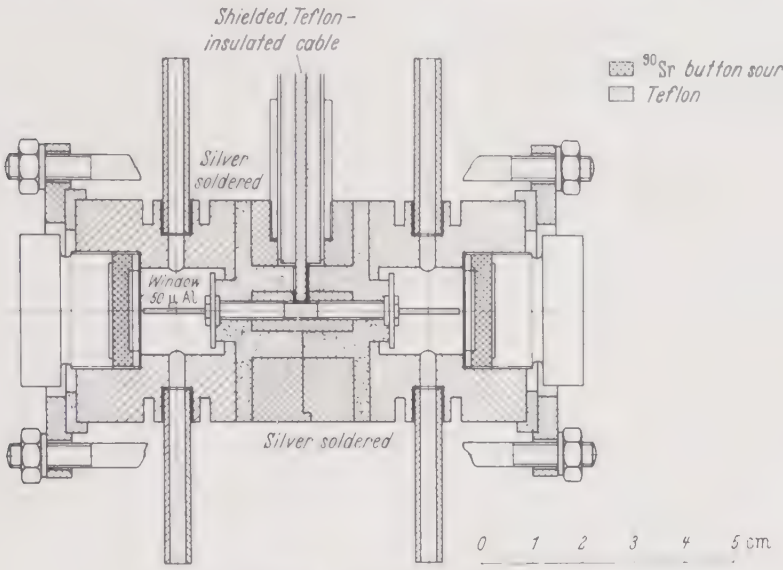

Figure 6. Beta ray detector cell

Figure 7. Photograph of β-ray detecting cells (prototype)

to the input of the recorder in order to filter out some of the high frequency noise. The time constant of the assembly should be some tenths of a second.

Figures 6 and *7* show the ionization cell in detail. Some recordings obtained with this system of detection are given in *Figures 8* and *9*.

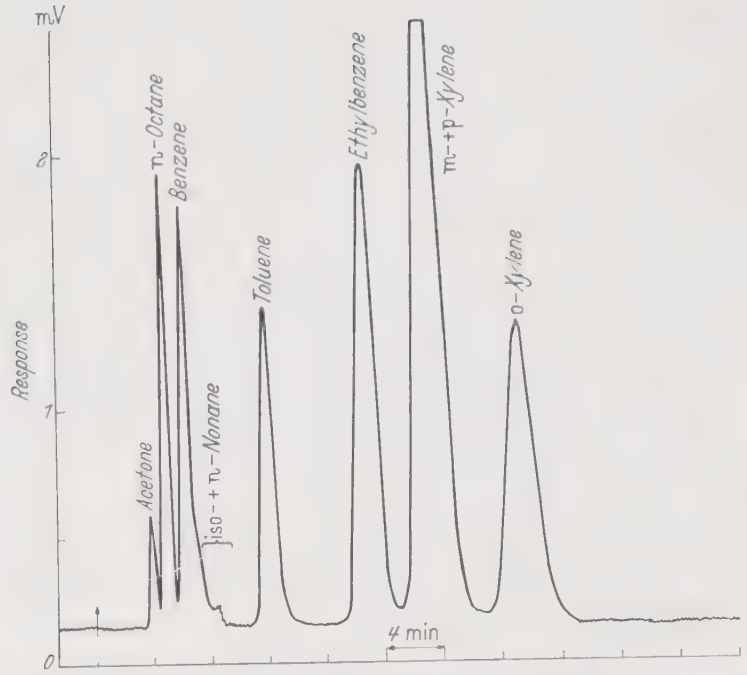

Figure 8. Gas–liquid partition chromatographic diagram of mixed aliphatics–aromatics. Liquid phase: mellitic acid ester. Detector: β-ray unit. Column packing: 40 parts liquid phase on 100 parts 'Sterchamol', 40–100 mesh. Column length: 180 cm. *Column temperature:* 118°C. *Carrier gas: nitrogen,* 2·6 litre/hour. *Sample size:* 2 mg

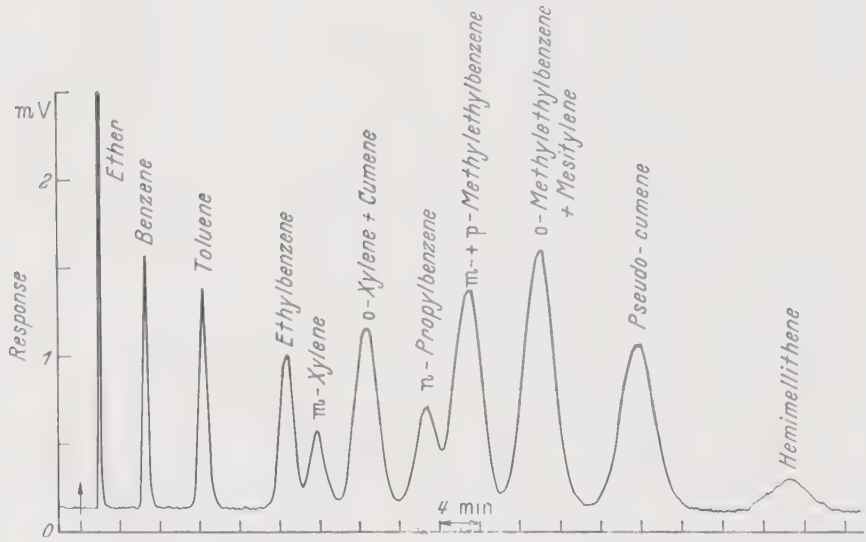

Figure 9. Gas–liquid partition chromatographic diagram of aromatic mixture. Liquid phase: naphthalene tetracarboxylic acid ester. Detector: β-ray unit. Column packing, length and temperature: as for Figure 8. Carrier gas: nitrogen, 2·6 litre/hour. *Sample size:* 4 mg, *exclusive of ether*

The author's thanks are due to Mr H. van Kranen for assistance in some of the experiments and to the management of the Koninklijke/Shell-Laboratorium, Amsterdam, for permission to publish this paper.

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DISCUSSION

H. Boer: In addition to my paper it may be useful to present the following comments.

Recently we have done some more work on the quantitative response of the β-ray detector. From this it follows that for the time being I have to disagree with Dr James as regards his remark that this detector requires appreciable calibration. The *Tables III*, *IV* and *V*, which give results on mixtures of different classes of

Table III. Quantitative Analysis of Mixture of Aromatic Hydrocarbons
Liquid phase: C_5–C_6 ester of dinitrodiphenic acid.
Temperature: 118°C. Hydrogen: 3·4 litre/hour.

Compound	*Percentage calculated from*				*Actual percentages*
	Uncorrected peak areas		*Corrected peak areas*		
Benzene	5·6	5·6	5·9	5·9	5·5
Toluene	5·7	5·8	5·8	5·9	5·6
Ethylbenzene	66·8	67·6	66·6	67·3	67·8
o-*Xylene*	11·6	11·2	11·6	11·2	10·8
p-*Methylethylbenzene*	10·3	10·0	10·1	9·8	10·3

hydrocarbons of widely varying boiling points and partly in rather diverse concentrations, show that fair results are obtained when making use of the ionization cross section data in question from the literature. Even if no corrections are made for ionization cross section, reasonably good results are obtained. It is evident that the duplicate results—which are not selected values—agree very well. Work on non-hydrocarbon compounds is in progress.

In the paper it is stated that the β-ray detector is adaptable to high temperatures. *Figure 10* shows the resolution of a mixture of aromatics and naphtheno-aromatics at a temperature of 255 C. It may be of interest to know that an ester is used here

as a fairly polar liquid phase. *Figures 11* and *12* give an idea of the separations that can be achieved with these liquid phases. The highest temperature at which the detector has been used is 280 C, the limit stated for Teflon. Still higher temperatures will require other insulating materials. We shall investigate this point further.

It has been suggested that the required high level of electrical insulation (better

Table IV. Quantitative Analysis of Mixture of Hydrocarbons. Liquid Phase: Dinitrodiphenic Acid Ester

Temperature: 199°C

Compound	Percentage calculated from				Actual percentages
	Uncorrected peak areas		Corrected peak areas		
n-*Decane*	3·9	3·9	3·5	3·4	3·6
cis *Decalin*	5·1	4·7	4·7	4·3	4·4
n-C_7-cyclo*Hexane*	4·2	4·3	3·7	3·8	3·8
n-*Pentadecane*	4·7	5·0	4·1	4·4	4·7
Naphthalene	67·5	67·4	69·8	69·8	69·0
Tri-n-C_3-*benzene*	5·3	5·3	4·9	4·9	5·1
Methylnaphthalene	9·3	9·3	9·4	9·5	9·4

than 10^{12} ohms) inside the cell would be upset by decomposition products from either the compounds to be detected or the liquid phase. This is seldom observed, as a matter of fact only when employing rather readily decomposing liquid phases. Proper functioning can be restored by injecting a few millilitres of a solvent such as acetone directly into the hot cell.

Table V. Quantitative Analysis of Mixture of Hydrocarbons. Liquid Phase: Dinitrodiphenic Acid Ester

Temperature: ←——101°C——→←——141°C——→

Compound	Percentages calculated from				Percentages calculated from				Actual percentages
	Uncorrected peak areas		Corrected peak areas		Uncorrected peak areas		Corrected peak areas		
Toluene	9·8	9·5	10·0	9·6	9·5	9·6	9·7	9·8	9·6
C_2-*Benzene*	29·5	29·6	29·4	29·5	29·6	29·8	29·5	29·7	29·9
o-*Xylene*	60·8	61·0	60·6	60·9	61·0	60·7	60·8	60·6	60·5

As regards the electronic part of the apparatus, the Honeywell–Brown Electrometer recorder has been found to be a very suitable instrument for recording the ionization current. It obviates the need of a separate d.c. amplifier. The input is shunted with about 10^9 ohms and a condenser of 100–1000 pF. The connection between the cell and the electronic apparatus has been made with shielded, Teflon-insulated cable of British Insulated Callenders Cables Ltd.

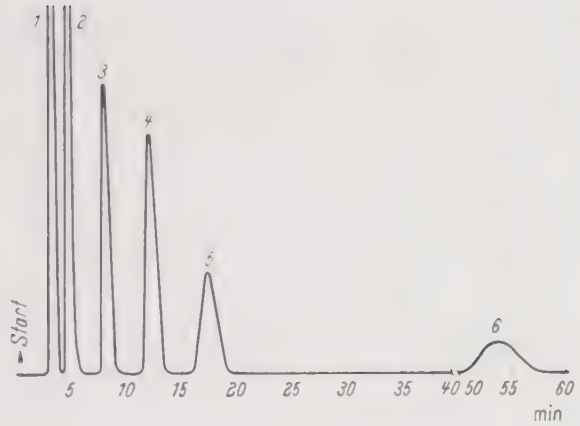
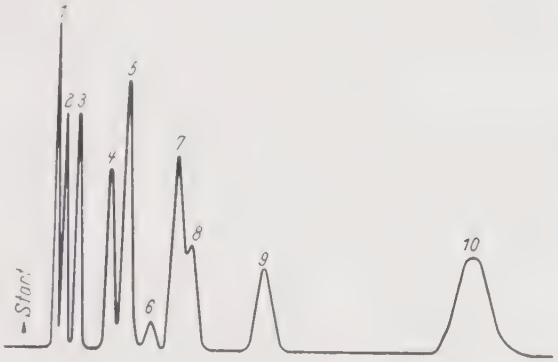


Figure 10. C_5–C_6 *ester of dinitrodiphenic acid.* 255°C. *Hydrogen:* 4·1 litre/hour

1, Tetralin 207°C;
2, Phenylcyclohexylmethane 242°C
3, Biphenyl 255°C;
4, asym-*Octahydrophenanthrene* 283°C;
5, sym-*Octahydrophenanthrene* 295°C;
6, Anthracene 355°C

Figure 11. C_5–C_6 *ester of dinitrodiphenic acid.* 200°C. *Hydrogen:* 4·1 litre/hour

1, trans*Decalin;*
2, cis*Decalin;*
3, 1-Methylindane;
4, Tetralin;
5, 2-Methyltetralin;
6, 6-Methyltetralin;
7, Naphthalene;
8, Benzothiophene;
9, 2-Methylnaphthalene;
10, 1:4-Dimethylnaphthalene



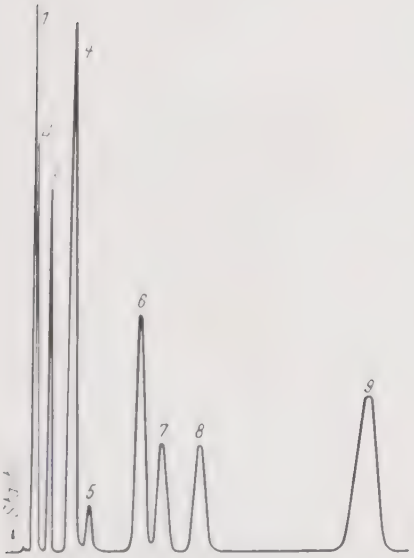


Figure 12. p-*Nitrobenzyl ester of dinitrodiphenic acid.* 200°C. *Hydrogen:* 3·5 litre/hour

1, trans*Decalin;*
2, cis*Decalin;*
3, 1-Methylindane;
4, Tetralin + *2-Methyltetralin;*
5, 6-Methyltetralin;
6, Naphthalene;
7, Benzothiophene;
8, 2-Methylnaphthalene;
9, 1:4-Dimethylnaphthalene

J. CHESHIRE: Referring to *Table I* (page 172) Dr Boer has said that he considers the response time of the β-ray detector is its most favourable property. As Dr Boer points out, the response time is controlled by the volume of the detector, but he has not attached much importance to this factor.

Two factors contribute to 'apparent efficiency':
(*1*) The first is obvious—column efficiency and the conditions under which it is run
(*2*) Rate of response of the detector.

The latter is the limiting factor during the first few minutes of close but quite well defined peaks. This rate of response is a function of the dead-space or inertia of the detector. Obviously the detector which can accommodate two peaks cannot be expected to resolve them. The hydrogen flame detector has a dead-space of less than 0·1 ml and fine thermocouple wires minimize thermal inertia.

Similarly recent developments of the thermal conductivity detector, such as Dr Keppler's glass cell (page 225), have a dead-volume as low as 0·2 ml. However, the dead-volume of the β-ray ionization detector is 2·8 ml and this must give rise to loss of apparent efficiency on the earlier peaks of any chromatogram.

H. BOER: I have to agree with Mr Cheshire that the dead-volume of the β-ray cell is about 2·8 ml, but I do not think this very high. As a matter of fact, as you can remember from *Table II*, in comparing narrow peaks with wide peaks the results are not affected at all. I think the response of the detector for these purposes seems to be fast enough, and we have found that even by running at fairly high temperatures and injecting mixtures of low boiling components, peaks will be obtained that practically return to the base line, provided the column does separate the components, of course. But we have never had any sign that the response of the cell with this dead-volume would affect the results.

C. L. DUNN: I would like to comment on experience in the U.S.A. with this equipment. I have been gone now ten months, but when I left there were about six or eight of these units in routine operation. One particular group adopted them in preference to other detectors because of their insensitivity to water in solution in organic solvents (65–75 per cent water). The β-ray instrument itself is in use for industrial purposes or plant control as a gas analyser independent of GLPC, so it has been proved to be a useful industrial instrument.

G. J. MINKOFF: I would like to take up this question of the volume of the detector and its effect on resolution. I think for quite a long time people did emphasize the need to keep it as small as possible, but I am not quite sure whether any actual work has been done to show the effect of, say, interposing a large volume between the column and the detector. I think Dr Ambrose found that when he went over to the thermistor-type detector instead of the katharometer—although there was a big diminution in size there was only a small increase in resolution—and we did one or two experiments in the Imperial College with katharometers in which we introduced quite a long piece of the glass tubing just to see if this decreased it. With our usual Ronsonol mixture we still got out the 25 peaks with no apparent change in resolution. I think perhaps that is a subject which calls for precise work, because in certain variations like the one that Mr Harrison described using the two columns alternately, quite a length of tubing is introduced. It is then vital to know whether one should try to make that up in fine steel capillary or whether one can just use ordinary glass tubing.

16

A THERMAL CONDUCTIVITY DETECTOR FOR USE AT HIGH TEMPERATURES IN VAPOUR PHASE CHROMATOGRAPHY

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'Shell' Research Limited, Thornton Research Centre

Hot-wire thermal conductivity bridges are widely employed to detect components in effluxes of vapour phase chromatograph columns and are called upon to operate at increasingly elevated temperatures as vapour phase chromatography is applied to materials of higher and higher boiling points.

Future widening of the scope of the method may well be hindered unless such detectors can be designed to operate at temperatures above the usual limit of 150–200 C. The difficulties involved, prominent amongst which is the prevention of gas leakage, will be discussed. Methods of surmounting them, exemplified in an instrument capable of reliable operation at 300–350 C, will be described with reference to testing and performance.

The high resolving power of gas–liquid partition chromatography is accompanied by concentrations of components in the column efflux which change rapidly and reach relatively high peak values. Instruments to detect these components must therefore respond rapidly and must be operated at temperatures high enough to prevent condensation. The temperatures demanded become higher and higher as progress is made in the analysis of more and more involatile materials. In addition there is always a need for maximum sensitivity and consequently for an extremely high degree of stability.

There has therefore been a revival of interest in the design of hot-wire thermal conductivity bridges, and the present paper describes the development of their construction to withstand temperatures up to at least 300° C—a value regarded as likely to satisfy demands in this respect for some time to come. Notwithstanding the tendency for physical properties other than thermal conductivity (e.g. density or beta ray absorption) to be used as the basis of detection, this development enables the study of other problems connected with high-temperature operation to proceed against a now very extensive background of experience with thermal conductivity detectors. Possible limitations of the latter, arising, for example, as a result of chemical or physical changes at the unusually hot surface of the wire, may also be studied.

To achieve the maximum rapidity of response, the thermal conductivity cell most commonly used in the present application has a straight hot wire suspended along the axis of a narrow-bore tube through which the gas sample

flows, and this is the type of cell to be considered. Following previous practice at lower temperatures a pure platinum hot wire 25 microns in diameter and 100 mm long in a tube of 3 mm diameter is employed. The column efflux passes through one such cell to a low-impedance liquid air trap which removes any sample components present, and then to a second identical cell; the two hot wires form arms of a Wheatstone bridge in the conventional manner to compensate for changes in their temperature other than those caused by variations of the composition of the gas in the first cell. At low gas pressures this compensation is inefficient unless both cells share substantially the same pressure. The design considerations which follow will be illustrated by imagining the hot wires, surrounded by pure nitrogen, to carry 100 mA in an equal-armed Wheatstone bridge connected to a high-impedance recorder having a range of 2·5 mV. An hourly stability well within 1 per cent of full scale deflection has been common under these conditions at temperatures up to 150–200°C.

Design Implications of High Temperature Operation

The problems of constructing thermal conductivity cells to withstand temperatures of 300°C and upwards are very largely those of choosing suitable materials, particularly for electrical insulation and gas seals. As insulators, only mica and ceramics are eligible; all other parts of the instrument must be of metals which retain the necessary physical properties up to, say, 350°C, joined where necessary by high melting point solders.

The degree of electrical stability required is illustrated by the fact that a change in wire resistance of only 5×10^{-4} ohm produces a recorder deflection of 1 per cent. Apart from the necessity to define extremely accurately the contacts at the wire ends (where an uncertainty of only 2 microns would cause this change of resistance) and the current paths to them, a shunt of about 2 megohms through insulation would result in the same recorder deflection. Fortunately, despite the enormously reduced resistivity of glass at 300°C, small Kovar-type glass-to-metal seals are quite adequate in this respect.

The temperature change of a wire to produce a 1 per cent deflection of the record amounts to about 4×10^{-3} °C. The traditional method of ensuring that both bores of the thermal conductivity bridge are accurately at the same temperature by forming them in a single block of copper must, however, be discarded as (apart from the inconvenience of its rapid oxidation at 300°C) copper will be shown to be unsuitable in other respects for use at high temperatures*. The necessity to use a material of lower thermal conductivity has occasioned no difficulty when the block is thermally isolated within a heated enclosure of high conductivity material such as copper or aluminium alloy.

The output of the bridge is also extremely sensitive to variations of tension in the wire, a change of strain of about 1×10^{-5} resulting in a 1 per cent recorder deflection. As the wire, which must be annealed for straightening, has to operate at temperatures approaching 500°C, it is important to stress it

* Cobalt beryllium–copper has interesting possibilities, however. It combines adequate hardness and heat resistance with an electrical conductivity of 50 per cent International Annealed Copper Standard and is said to oxidize more slowly and to machine satisfactorily. The disadvantage of a relatively high coefficient of expansion remains.

as lightly as is consistent with avoidance of sag and microphony. The resilient wire mounting commonly incorporated in instruments designed for ordinary temperatures must therefore be adapted to accommodate larger differences between the expansions of wire and block, and there is a considerable advantage in matching their expansion coefficients.

Design of this mounting must take account of the requisite accurate radial location of the wire. From the conductive heat transfer coefficient per unit length, C, between a bore of radius b and wire of radius a situated parallel

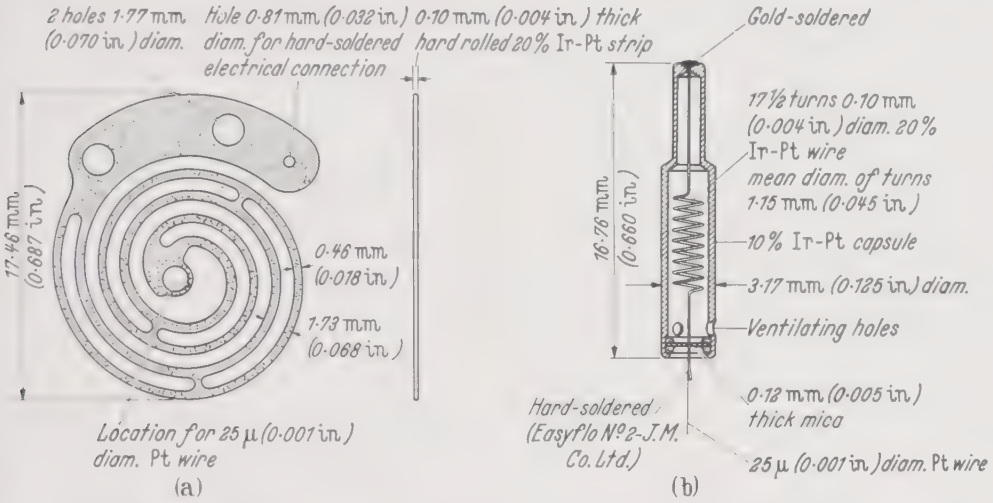
2 holes 1·77 mm (0·070 in.) diam.
Hole 0·81 mm (0·032 in.) diam. for hard-soldered electrical connection
0·10 mm (0·004 in.) thick hard rolled 20% Ir-Pt strip
17·48 mm (0·687 in.)
0·46 mm (0·018 in.)
1·73 mm (0·068 in.)
Location for 25 μ (0·001 in.) diam. Pt wire
(a)
Gold-soldered
17½ turns 0·10 mm (0·004 in.) diam. 20% Ir-Pt wire
mean diam. of turns 1·15 mm (0·045 in.)
16·76 mm (0·660 in.)
10% Ir-Pt capsule
3·17 mm (0·125 in.) diam.
Ventilating holes
0·12 mm (0·005 in.) thick mica
Hard-soldered (Easyflo No 2-J.M. Co. Ltd.)
25 μ (0·001 in.) diam. Pt wire
(b)

Figure 1. Resilient mountings for hot wires of thermal conductivity cells: (a) *flat spiral form* (*rate* 20 g/cm); (b) *encapsuled helical form* (*rate* 40 g/cm)

with and at a distance d from the axis of the bore, in a gas of conductivity K, given by

$$C = 2\pi K/\cosh^{-1}\{(a^2 + b^2 - d^2)/2ab\}$$

one estimates that a displacement of about 25 microns from exact concentricity will cause a recorder deflection of 1 per cent. Matters rapidly become worse if the wire is initially eccentric. For these reasons a simple helical spring was considered to be unsuitable, and two forms having better radial rigidity were designed. Both are of iridium–platinum, which in addition to retaining excellent elastic properties at 300°C has the important advantage of hard-soldering easily with a minimum of flux. The flat spiral form shown in *Figure 1* (a) has a rate of 20 g/cm and in conjunction with a Dural block limits the variation of wire tension throughout the entire range of operating conditions to about 1 g. It was engraved from heavily copper-plated iridium–platinum sweated to a substantial brass base, the copper being necessary to prevent attack by the soft solder. There are practical difficulties in achieving so weak a spring of the encapsuled helical form shown in *Figure 1* (b). This has a rate of 40 g/cm which in conjunction with a stainless steel block limits the total variation of wire tension to about 0·5 g. It must be stabilized before assembly by heating for about an hour to the maximum operating temperature under the maximum working tension. Where the higher rate is acceptable, the second form of spring avoids the necessity for

gasketed seals of large diameter, and makes it easier to place the tubes close together.

Prevention of gas leakage past electrical leads, pipe connections, and the closures of other constructionally necessary openings has presented the most difficult design problem, as the instrument is required to operate at pressures below atmospheric and also the carrier gas may be hydrogen. Considering the effect on thermal conductivity, the leakage of air into hydrogen flowing at 1 litre/hour (s.t.p.) estimated to cause a 1 per cent recorder deflection is about

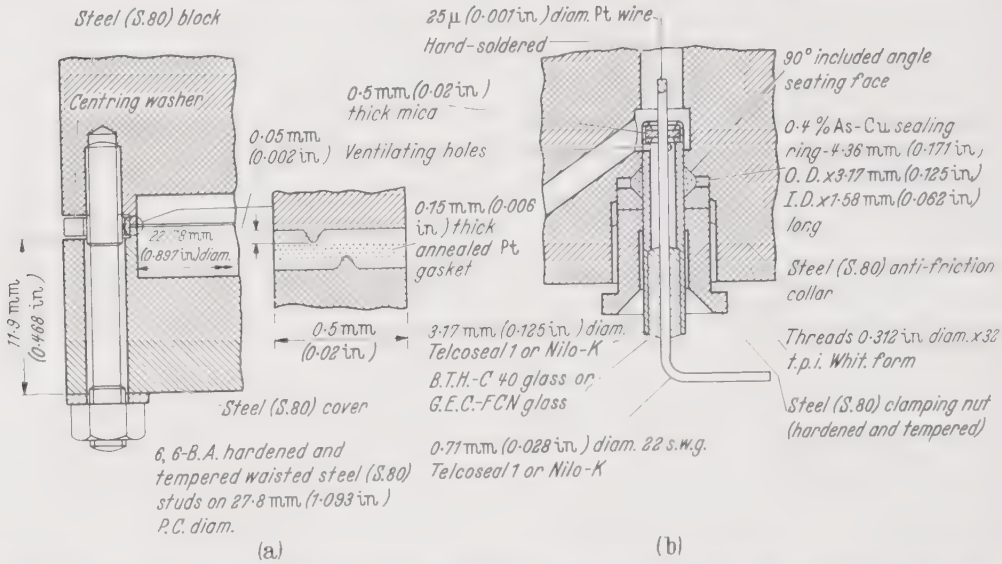
Steel (S.80) block
Centring washer
0·05 mm (0·002 in.)
0·5 mm (0·02 in.) thick mica
Ventilating holes
22·78 mm (0·897 in.) diam.
11·9 mm (0·468 in.)
0·15 mm (0·006 in.) thick annealed Pt gasket
0·5 mm (0·02 in.)
Steel (S.80) cover
6, 6-B.A. hardened and tempered waisted steel (S.80) studs on 27·8 mm (1·093 in.) P.C. diam.
(a)
25 μ (0·001 in.) diam. Pt wire
Hard-soldered
90° included angle seating face
0·4 % As-Cu sealing ring-4·36 mm (0·171 in.) O.D. x 3·17 mm (0·125 in.) I.D. x 1·58 mm (0·062 in.) long
Steel (S.80) anti-friction collar
3·17 mm (0·125 in.) diam. Telcoseal 1 or Nilo-K
B.T.H.-C 40 glass or G.E.C.-FCN glass
0·71 mm (0·028 in.) diam. 22 s.w.g. Telcoseal 1 or Nilo-K
Threads 0·312 in. diam. x 32 t.p.i. Whit. form
Steel (S.80) clamping nut (hardened and tempered)
(b)

Figure 2. Demountable metal-to-metal gas seals: (a) *large diameter covers (platinum gasket);* (b) *small diameter cylindrical inserts (arsenical copper sealing ring)*

5×10^{-3} lusec (litre micron per second). The same leakage supporting catalytic combustion at the surface of the wire (which in hydrogen may be expected well below the maximum wire temperature) might have an effect many times greater. It is evidently prudent to aim at seals which are leak-free in the high-vacuum sense. They must also be renewable without too much difficulty when the cells have to be dismantled.

All-metal Demountable Gas Seals

Many experiments indicate that the general principles of good metal-gasketed seals are as follow:

(*1*) The clamping faces must be true, well finished, and much harder than the gasket. They should be amply supported and, if large diameters are unavoidable, stress-relieved.

(*2*) The gasket material must deform plastically to a work-hardened state and must not anneal below the maximum working temperature.

(*3*) The profile of either the clamping faces or the gasket must be such that on both sides of the latter there is at least one continuous track of severe deformation penetrating beneath surface defects in the gasket.

(*4*) The resilience, dimensions, and expansion coefficients of the seal components must be so chosen that the gasket remains under well distributed compression throughout the working temperature range.

These principles are exemplified in the seal shown in *Figure 2* (a), which is a form suitable for enclosing wire anchorages embodying the flat spiral spring illustrated in *Figure 1* (a). The combination of a fully annealed thin platinum gasket between stainless steel clamping faces has proved the most reliable of many tried.

For sealing cylindrical inserts up to at least 3 mm diameter, such as pipe connections, spring capsules as shown in *Figure 1* (b) and tubular glass-to-metal seals, the 'Simplifix' type of construction shown in *Figure 2* (b) has been entirely successful. Its essential feature is the employment of 0·4 per cent arsenical copper for the sealing ring; this does not anneal at the maximum working temperature, whereas with unalloyed copper leaks invariably develop from this cause.

Several cells incorporating these types of seal have been made which have had aggregate leaks, when hot and cold, consistently below 1×10^{-2} lusec, and showing no tendency to increase after as many as ten cycles between 50 and 300°C.

Thermal Conductivity Bridge for Use at 300°C

A thermal conductivity bridge designed to work at temperatures up to at least 300°C is shown in *Figures 3* and *4*. To provide adequately hard sealing faces, to match as closely as possible the expansion coefficient of platinum, and to resist corrosion, the block is of stainless steel (S.80). For simplicity, demountable seals are avoided where possible by hard-soldering the gas connections at joints which can be made without heating the block as a whole. The form, shown in *Figure 2* (b), of the rigid insulated wire anchorages is dictated by the necessity to locate the hot wires accurately on the axes of the bores and to protect the glass from the compression of the sealing ring. One end of the platinum wire is embedded in Easyflo 2 solder (m.pt 608–617°C; Johnson Matthey & Co. Ltd) contained in a minute conical depression cut in the end of the central support so as to be accurately on the axis of the outer member of the glass-to-metal seal. The other end of the wire is accurately aligned with and hard-soldered to the inwardly projecting tail of the helical spring; at this stage the spring is not yet attached to its capsule. The spring assembly is lowered down the bore and seals are fully tightened in their proper positions. By means of a spring balance, the outwardly projecting tail of the spring is then subjected to a tension of 1 g and after careful alignment with the axis of the bore is gold-soldered to its capsule. If the necessary heat is applied as locally as possible the capsule and seal keep the coils of the spring adequately cool. Gold-soldering, and therefore an iridium-platinum spring capsule, are adopted to ensure reliability, and in particular to avoid flux, in this vital final operation which can be inspected only from the outside. The tension of the filament can, however, be checked by determining its natural frequency of transverse vibration by the method shown in *Figure 5*. A magnetic field is applied across the wire in question, and the bridge is balanced. A small alternating current of adjustable and known frequency is then superimposed on the bridge supply, exciting forced transverse oscillations of the wire. At the appropriate frequency (in the present case 150 c/s) resonance occurs and is recognizable by a sharp disturbance of the bridge balance as a result of the increased heat dissipation

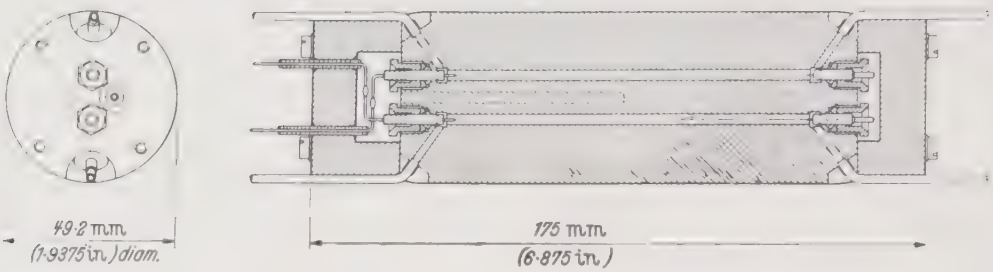

Figure 3. Hot wire thermal conductivity bridge; cross section showing construction

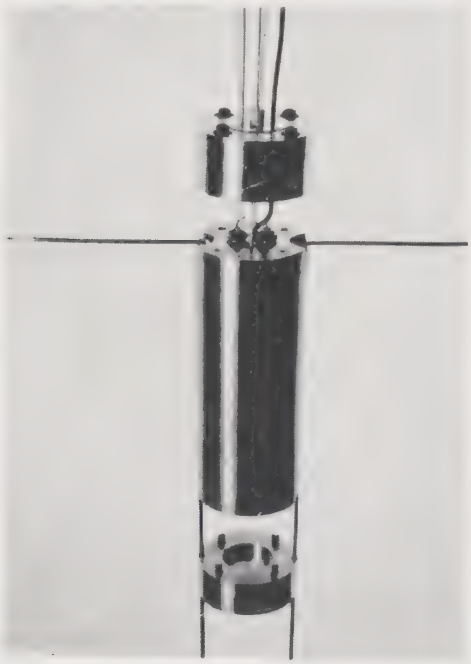

Figure 4. Hot wire thermal conductivity bridge for operation at 300°C; covers raised to show electrical connections

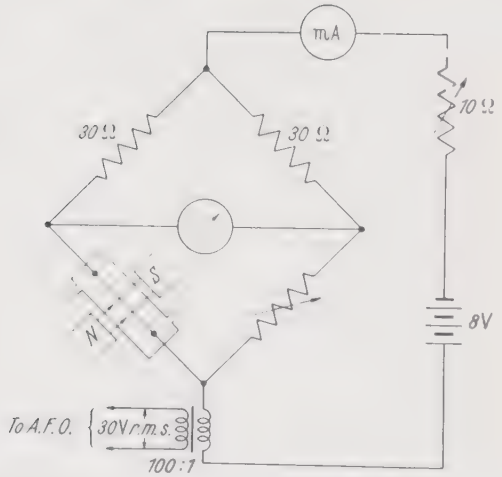

Figure 5. Method of determining hot wire tension in assembled thermal conductivity cell

caused by motion of the wire. With blocks of non-ferrous material, a small permanent magnet serves to provide the magnetic field, but with the present stainless steel block a rather powerful electromagnet had to be used.

Stability and Sensitivity at 300°C

The record shown in *Figure 6* was obtained at 300°C with a detector as shown in *Figures 3* and *4*. The sample gas was nitrogen saturated with the vapour of refrigerated acetone.

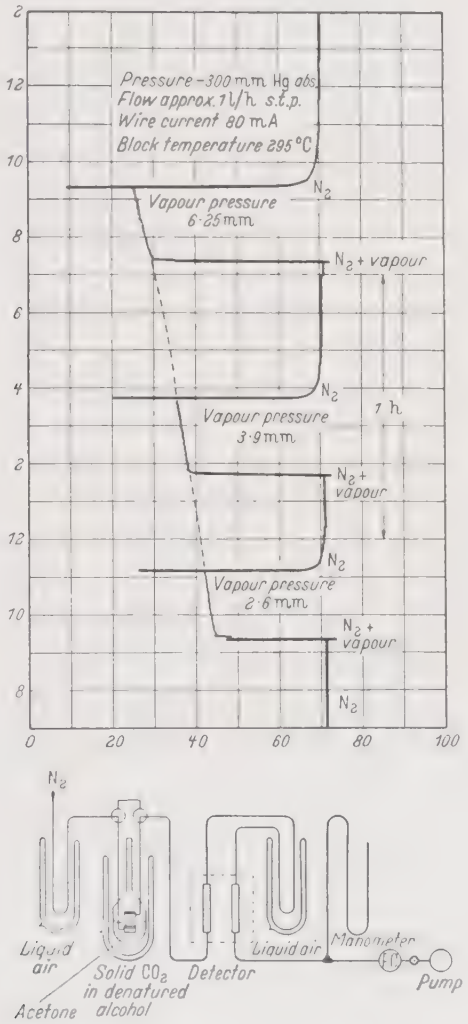

Figure 6. Stability and sensitivity of katharometer operating at 300°C

The record follows the slowly rising acetone temperature and returns to the base line when the saturator is by-passed. This has proved a useful method of sensitivity measurement. In contrast with its effect at room temperatures, the presence of acetone vapour reduces the hot wire temperature. The satisfactory return to the base line indicates that no serious irreversible change of the wire surface has occurred in this case.

Thanks are due to the Directors of 'Shell' Research Limited for permission to publish this paper, and to Mr J. Nicholson for invaluable help and advice on workshop matters.

DISCUSSION

L. Blom: I should like to draw your attention to another possibility of detection which I used for several years and which was published in *Analyt. chim. Acta* **18,** 120, 1955. This method is extremely simple and although it is not applicable to all problems, it may be very useful for those who need an inexpensive apparatus.

The method, like others, is based on combustion over copper oxide. However, the carbon dioxide formed is titrated directly in a simple glass apparatus with pyridine as a solvent and sodium methylate dissolved in pyridine–methanol mixture (4 : 1) as a titrant. With this method you need no calibration if the substances are known and you find the total mass of each component immediately. Further, you need no accurate control of the gas velocity. The sensitivity and accuracy are satisfactory. Amounts of 1–10 mg of sample mixture are analysed and a few microgrammes of each single component may be found in the exit gas. The method was applied to a wide variety of organic substances, including nitrogen-, sulphur- and halogen-containing ones.

For work at high temperatures (250°C) the oxygen needed for the combustion is introduced behind the separation column.

G. A. P. Tuey: We have been using gas chromatography for some time for the examination of substances boiling in the range 200–300°C and have experienced most of the difficulties already referred to, such as instability of the detector system and lack of sensitivity.

It seemed to us that the usual arrangement of katharometer cells in the inlet and outlet gas streams failed to achieve the differential action which it is often inferred to give. The inlet and outlet gas streams are at different temperatures and pressures and have different flow rates; fluctuations in the inlet stream cause only minor fluctuations in the outlet stream because of the throttling effect of the column packing.

We therefore adopted a dual column arrangement, the two columns being identical in packing and each having an inlet and outlet katharometer. The four katharometers form the Wheatstone bridge detector network and give complete balancing of flow disturbances. Since all the arms of the Wheatstone bridge are kept at the same temperature by the vapour jacket surrounding columns and katharometer, no drift is produced by ambient temperature changes as when two arms consist of ordinary fixed resistances.

The sensitivity of the katharometer has been raised by the use of a zig-zag arrangement of wires tensioned between spring-loaded Teflon supports. This enables about 40 cm of wire to be used in a cell 13 cm long; the sensitivity is about three times as great as with a 10 cm wire.

The arrangement of tubes is in the form of a ∩ with the packing in one vertical limb. The other (inlet) limb can be filled with a granular packing moistened with the stationary phase used in the main column, and then acts as a preheater and saturator for the nitrogen supply as suggested by Dr Glueckauf. The katharometer is constructed entirely of Monel metal with Teflon gaskets and insulators.

The apparatus has been extensively used for the examination of halogenated phenols and high-boiling esters; its stability may be judged from a chart from the 2 mV recorder which shows no discernible variation during 70 minutes at an operating temperature of 212°C.

A. J. Davies: Perhaps Dr Tuey's statement that under dynamic conditions there is no heat transfer from the hot wire to the bore of a katharometer should not go unchallenged.

If, as in some forms of katharometer, you have the bore in the form of an insert

in a thermostatted block, the rise of the temperature of the wall of the tube can be very easily measured under the ordinary kind of wire loading to be as much as 1C°.

As regards the question of wire concentricity, we do not want to stress this overmuch. Our philosophy in the design of this instrument was to eliminate all possibilities where in principle trouble could occur, and hence how it could be done without too much trouble. It was particularly important that for operation at low pressures we did our best to make the wires concentric.

17

A LARGE SCALE ANALYTICAL GAS-LIQUID PARTITION CHROMATOGRAPHIC UNIT

B. T. WHITHAM
'Shell' Research Limited, Thornton Research Centre

Details of construction and operation of a larger scale analytical gas–liquid partition chromatographic unit are described. With a column of 830 cm length and 12·7 mm internal diameter sample sizes of up to several millilitres of liquid have been separated. Some applications of this unit in the analysis of complex petroleum fractions and for preparative purposes are described.

Gas-liquid partition chromatography (GLPC) is primarily a batchwise method of separation, which is rapid and selective enough to be used as a self-supporting method of analysis for a wide range of substances. However, in many applications in the analysis of petroleum it is necessary to use GLPC in conjunction with other analytical techniques such as spectroscopy, and in these circumstances columns capable of separating up to millilitre quantities of liquid samples are sometimes required. The small analytical GLPC units can be used to isolate constituents from complex mixtures for identification by mass spectroscopy, but sometimes the separation is insufficient and the isolation of minor constituents in the sample is difficult. Generally the amounts of sample which can be handled in such units are unsuitable for investigation by methods other than mass spectroscopy.

Prefractionation of wider range petroleum mixtures prior to analysis of the fractions on smaller analytical GLPC units using column stationary phases of different selectivity is an application of larger columns which will be described. A GLPC column which can satisfactorily separate millilitre quantities of sample also becomes important for isolating small quantities of pure substances for calibration purposes and research work.

There is little information available on the operation of larger GLPC columns but Bradford *et al.*[1] mentioned the use of a column of increased diameter taking half-millilitre liquid samples for the separation of hydrocarbons. Any decrease in separating power was stated to be overcome by running samples at lower column temperatures. James and Martin[2] have used columns of 350 cm length and mentioned the possibility of employing very long columns for difficult separations[3]. Recently Lichtenfels *et al.*[4] have described the use of a 425 cm column and Groenings *et al*[5]. a 1524 cm column for separating hydrocarbon mixtures.

The unit described in this paper was constructed to operate with GLPC columns of various dimensions but up to the present time only one size of column has been used. This was designed to combine a high separating power for small sample sizes with a capacity to separate larger samples when required.

Description of Large Scale Analytical GLPC Unit

The general layout of the equipment is shown diagrammatically in *Figure 1*. As with the small analytical units used in the author's laboratory, the gas was generally drawn through the column by a vacuum pump with the pressure on the inlet side about atmospheric. The control of pressure and flow was by means of two oil-damped valves and a needle valve arranged as shown in *Figure 1*. In experiments with hydrogen as carrier gas, pressure was applied at the column inlet to drive the gas through the column, the outlet being at

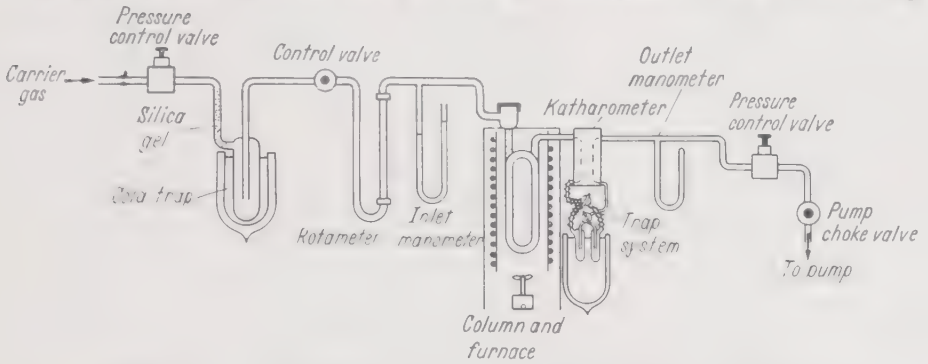

Figure 1. Flow diagram of large scale analytical GLPC apparatus

atmospheric pressure. This arrangement was found to give better stability with this gas. The more important features of the unit are described below.

Column

Although coiled columns could have made the unit more compact it was considered preferable to use straight columns with U-bends since loss in efficiency has been noted for wide columns (>10 mm) of the former type. The column consisted of two glass U-tubes, of 12·7 mm internal diameter connected by a U-bend of the same diameter. The overall length was 830 cm (see *Figure 2*). Gas connections to the inlet and outlet of the column were by means of metal–glass flange joints with 'Teflon' seals. The first 4 cm of the column was packed with glass-wool and heated by means of a small auxiliary electric heater which was wound round the outside of the column. The winding of this heater was continued for another 10 cm down the outside of the column, but these lower windings were spaced considerably so that the temperature of this part of the column was only slightly above that of the furnace in which the column was enclosed. The temperature of the auxiliary heater was measured by means of a thermocouple. As already noted the dimensions of the column were chosen with two objects. First, to have available a column of high separating power for small sample sizes and, secondly, a column capable of separating larger sample sizes with a reasonable degree of efficiency. The length of the column was arbitrarily chosen as 830 cm and the diameter approximately double that of the small analytical columns in use in the author's laboratory.

Furnace and temperature control

The column was heated in an electric furnace with forced air circulation from a fan situated at the base (see *Figure 3*). The temperature was adjusted and

controlled by means of an automatic on–off controller operating from a thermocouple. The overall heat input was adjusted by means of a Variac. The furnace was 7 feet long and 5 inches in diameter. The temperature variation was $\pm\frac{1}{2}$C° at 150 C and the temperature difference between the top and bottom of the column was about 5C°, the greater proportion of this

Figure 2. 830 cm *column assembly for large scale analytical GLPC apparatus*

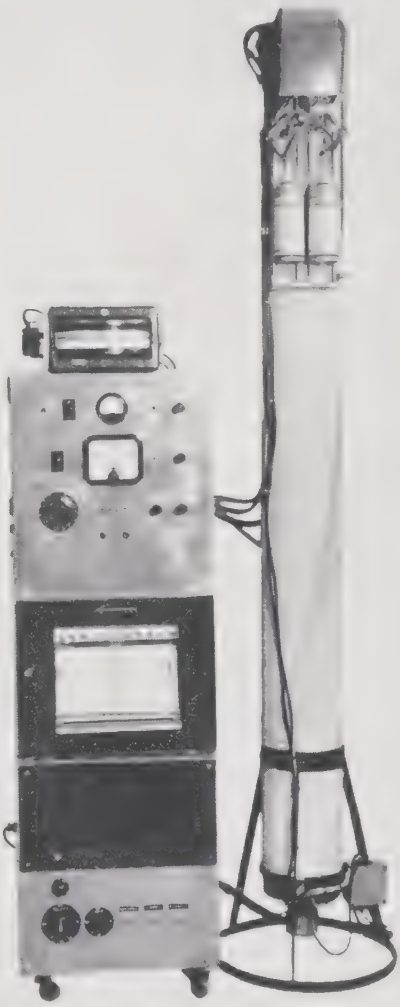

Figure 3. Large scale analytical GLPC apparatus. General view showing furnace and control unit

gradient being in the last 6 inches of the furnace. The maximum operating temperature was 300 C. The furnace had a certain degree of flexibility in that temperatures could be changed during a run if required. The column could be removed by disconnecting the gas and electrical connections and then sliding the mounting spigot of the column out of the furnace.

Detector

A thermal conductivity cell (katharometer) was used as detector and this consisted of two parallel chambers $\frac{1}{8}$ inch diameter in a copper block $5\frac{1}{4}$ inches

long and 2½ inches diameter. The platinum elements were 50 s.w.g. wires supported at one end by springs of platinum–rhodium wire. The katharometer was sealed with silicone rubber gaskets enabling it to be run at temperatures up to 170 C. It was mounted on the outside of the furnace and enclosed in an aluminium cover. Heating was by means of an electric tape wound round the outside of the copper block. The heat input was manually controlled by means of a Variac and the temperature checked by means of a thermocouple. The full gas flow from the column was taken through the cells of the katharometer.

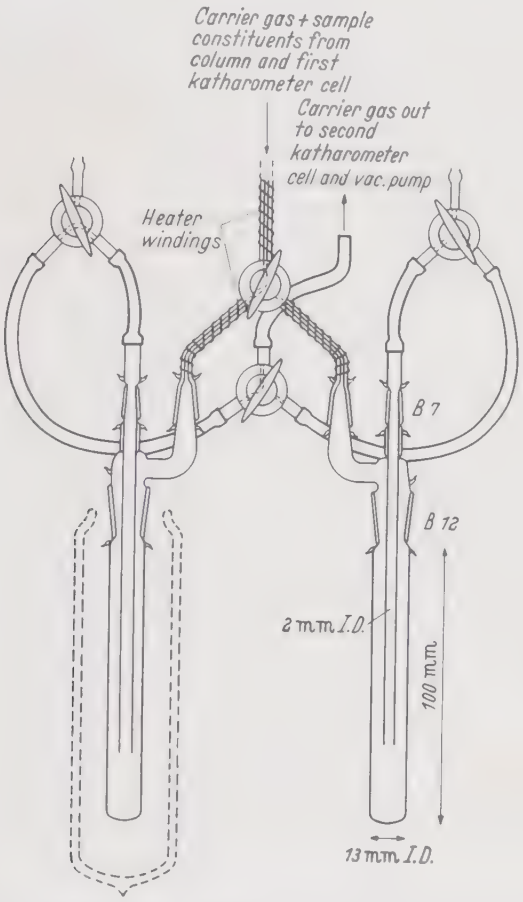
Carrier gas + sample constituents from column and first katharometer cell
Carrier gas out to second katharometer cell and vac. pump
Heater windings
B 7
B 12
2 m.m. I.D.
100 m.m.
13 m.m. I.D.

Figure 4. Trap system for large scale analytical GLPC unit

Trap system

This was a simple arrangement of two traps with two three-way taps so that the gas flow could be diverted from one trap to the other. The gas lines from the katharometer to the traps were heated by an electric heater to avoid condensation (see *Figure 4*). It was found advantageous to have the trap system located between the two katharometer cells, since the failure of a constituent to condense or blockage of the trap was immediately recorded on the recorder chart by a negative deflection. The traps themselves were quite simple in design. It would be advantageous to have a somewhat wider central tube, because blockage can occur with low boiling substances. Liquid air was

invariably used as the freezing liquid and in a series of tests it was shown that reasonable recoveries were obtained (see below under *Operating conditions*). Two further three-way taps were situated in the gas lines to enable the vacuum to be released when changing traps.

Recording and control unit

The various controls for the furnace, auxiliary heaters, gas control valves, manometers, rotameter and vacuum pump, were incorporated in a light framework and control panel mounted on wheels (see *Figure 3*). An a.c. rectifier and current stabilizer, to supply the Wheatstone bridge circuit of the katharometer, was also mounted in this framework together with a 2·5 mV recorder fitted with a manually controlled sensitivity switch. A multipoint temperature indicator enabled the various thermocouple temperatures to be noted. All electrical and gas connections to the furnace, column, and detector unit could be quickly released when it became necessary to isolate the recording and control unit in order to change the column.

Operating Features

Column stationary phase

In order that the greatest efficiency may be obtained from long columns it is essential that the ratio of the inlet to outlet pressure should not be too high, so that there is no wide variation in gas velocity. Consequently, the use of fine particle supports like diatomaceous earth is often unsatisfactory and an alternative has been found in ground furnace brick[6]. The most suitable grade of furnace brick so far used is one manufactured in Germany under the trade name 'Sterchamol', although it is understood that C22 firebrick manufactured by Johns Manville is also suitable. A brick similar to Sterchamol but manufactured in the U.K. was found to be unsatisfactory in the column because of poor retention of the liquid phase. It was found, after a number of particle sizes had been tested, that the best mesh size to use in a column of the dimensions described in this paper was 44–52 mesh, but a somewhat wider range is to be preferred from the point of view of economy. There is a sharp fall in efficiency for particle sizes below 30 mesh. The pressure drop across the column packed with 44–52 mesh Sterchamol brick coated with 26 per cent weight silicone fluid M.S.550 at 110°C, for a nitrogen flow rate of 4 litres per hour, was 550 mm of mercury.

The stability and non-volatility of the liquid stationary phase becomes of greater importance with large columns than with small columns. At the present time silicone fluid M.S.550 has mainly been used as the liquid stationary phase because of its effectiveness over a wide temperature range. This is a mixed phenyl–methyl siloxane and has behaved satisfactorily in the small analytical columns up to temperatures of 220 C. However, in the large column small amounts of the fluid tend to accumulate in the lines from the katharometer to the traps at column temperatures above 150 C. Also trace contamination of fractions with benzene has been noted after columns have been in operation for some time. Thus the choice of liquid stationary phases to give satisfactory operation in larger GLPC columns will be more limited than for the smaller analytical units.

Operating conditions

Outlet pressure has generally been between 80 and 200 mm of mercury with flow rates varying between 4 and 8 litres per hour of nitrogen. Lower flow rates can be used for particularly difficult separations. With flow rates of nitrogen in the region of 10 litres per hour, a certain amount of instability becomes evident in the base line of the recorder, but the reason for this has not been discovered. Tests were carried out with a sample of toluene and *iso*octane and, with a 3 ml column charge, overall recoveries of 97·5 per cent were obtained in the traps with an outlet pressure of 80 mm of mercury.

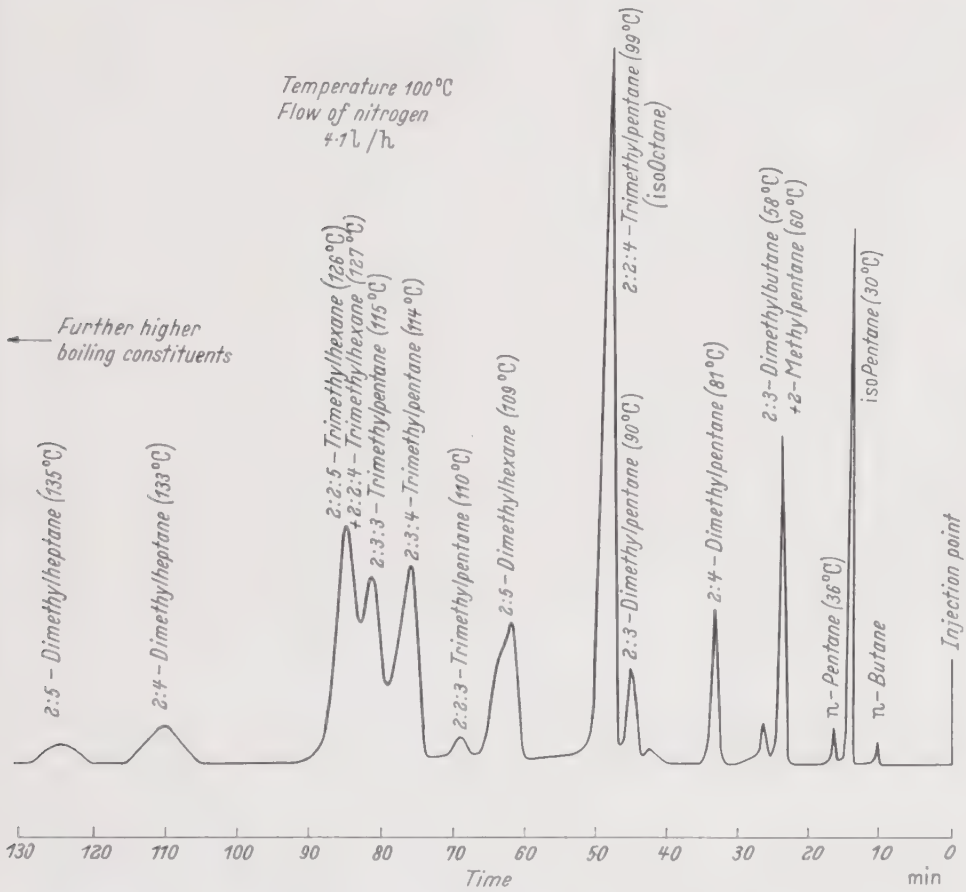

Figure 5. 4:4-Alkylate 0·06 ml. *Large scale analytical GLPC unit.* 830 cm *column. Silicone fluid M.S. 550 stationary phase on 44–52 mesh 'Sterchamol' brick*

Lower boiling substances fail to condense completely under the above conditions and higher outlet pressures are more satisfactory in these cases. With small sample sizes of about 0·1 ml, complete condensation of low boiling substances is generally satisfactory. The two-trap system has been found to be satisfactory even when several constituents are being condensed from a sample, since generally there is ample time to change a trap while a constituent is being condensed in the second trap.

Samples are introduced into the column through a rubber serum cap on to the glass-wool plug at the column inlet by means of a hypodermic syringe

fitted with a long needle. The temperature of this glass-wool plug is maintained at least 30C° above the boiling point of the highest boiling substance in the sample being introduced. This method has been found satisfactory for sample sizes up to 3 ml, and separation was little improved by higher vaporization temperatures. It is possible that some form of separate vaporizer will be more satisfactory for larger samples.

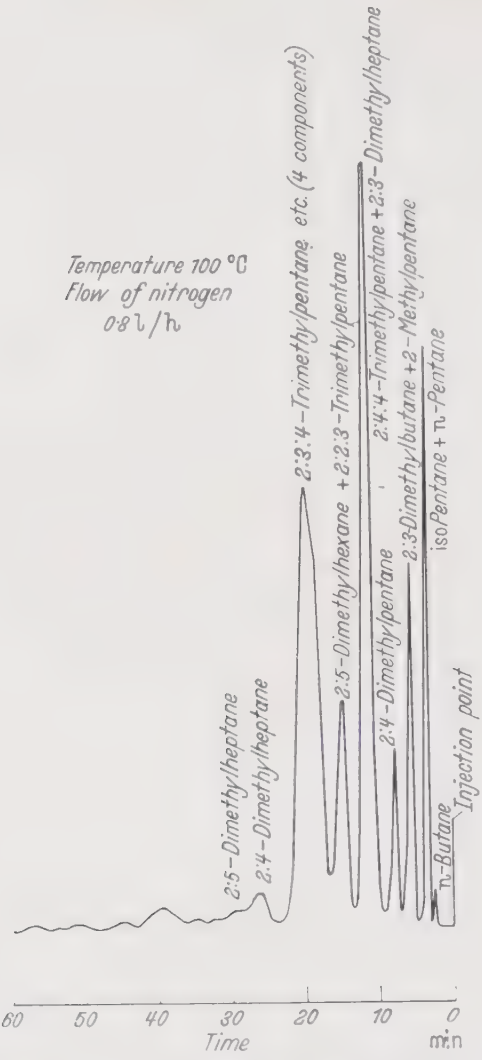

Figure 6. 4:4-Alkylate 0·01 ml. *Normal analytical GLPC unit.* 184 cm *column. Silicone fluid M.S. 550 stationary phase on Celite 545*

Efficiency and separating power

The efficiency of the large scale column has not been related to that of the small 184 cm × 6 mm internal diameter analytical columns used in the author's laboratory under operating conditions which can be considered exactly comparable. However, the apparent numbers of theoretical plates for the two columns have been determined using toluene (see *Table 1*). The columns were operated so that flow rates were 6·5 and 0·8 litres per hour and the liquid phase supports were respectively ground furnace brick of

44–52 mesh and Celite 545 (fines removed). It will be noted that when the sample size in the large column is four times that in the smaller the number of plates per centimetre length of column is approximately the same. The greater length of the large column enables better separations to be obtained and this is illustrated with a sample of 4:4-alkylate* when a small sample size is used (see *Figure 5*). The separation achieved with this sample on the small analytical column using the same liquid stationary phase, column temperature and outlet pressure with a flow rate approximately one fifth that in the large column is shown in *Figure 6*. The sample size in the small column

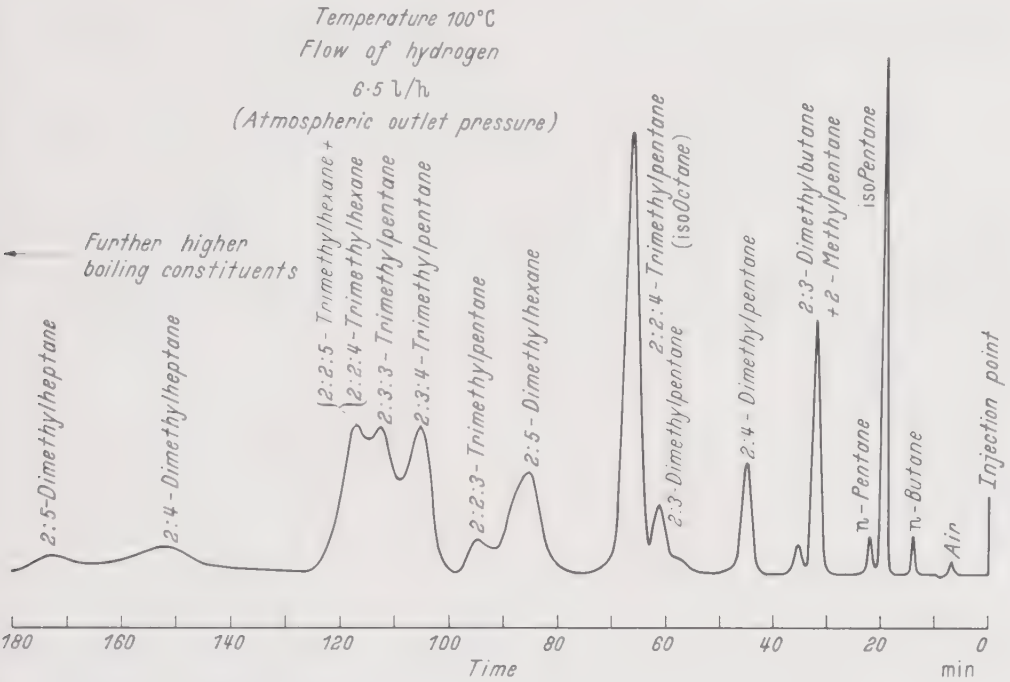

Figure 7. 4:4-Alkylate 0·001 ml. *Large scale analytical GLPC unit.* 830 cm *column. Silicone fluid M.S. 550 stationary phase on 44–52 mesh Sterchamol brick*

was slightly under half that normally used. It can be seen that quite a number of the constituents of the alkylate separated on the large column are unresolved on the small one.

An experiment was carried out on the large column with hydrogen as the carrier gas and increasing the katharometer current to obtain a sensitivity of approximately 60 times that with nitrogen. This enabled a sample size of 0·001 ml to be used and the trace obtained is shown in *Figure 7*. It will be noted, however, that the separation is little different from that with nitrogen at 0·06 ml sample size.

When using the large unit for preparative purposes the amount of sample which can be charged depends very much upon how well separated the

* 4:4-Alkylate is a petroleum product consisting of a mixture of highly branched paraffin hydrocarbons prepared by the reaction of *iso*butane and *n*-butylene in the presence of a catalyst.

Table 1. Apparent Plate Efficiencies of Analytical GLPC Units with Silicone Fluid M.S. 550 Liquid Stationary Phase

Quantity	*Normal analytical GLPC units* 184 cm × 6 mm *I.D. column*	*Large scale analytical GLPC unit* 830 cm × 12·7 mm *I.D. column*
Apparent number of theoretical plates at 100 C *for toluene**	407(0·025 ml†) 773(0·006 ml)	1967(0·10 ml) 3743(0·025 ml)
Number of theoretical plates per cm *of column for toluene*	2·2(0·025 ml) 4·2(0·006 ml)	2·4(0·10 ml) 4·5(0·025 ml)

* Calculated by the method of James and Martin[3], i.e. apparent no. of plates = $2\pi(hl/a)^2$ where h = peak height l = retention distance, and a = peak area.

† Sample size.

required constituent is from the remaining substances in the sample. For two constituents present in equal proportions and boiling 5C° apart it is possible to separate completely about 2·3 ml of the mixture. The separation of a 2 ml sample of equal proportions of *o*- and *p*-xylene is shown in *Figure 8*.

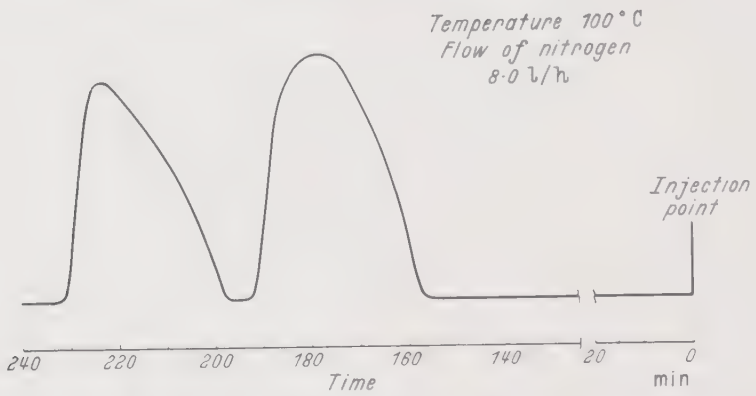

Figure 8. Separation of 2 ml *sample of* o- *and* p-*xylene. Large scale analytical GLPC unit.* 830 cm *column. Silicone fluid M.S. 550 stationary phase on 44–52 mesh Sterchamol brick*

By utilizing a more selective liquid stationary phase, even larger quantities of these aromatics could be separated.

Applications of the Unit in the Analysis of Petroleum

The technique of identifying and determining substances in complex mixtures by a combination of GLPC separation and mass-spectroscopic examination of the fractions has been described by Bradford *et al.*[1]. This has proved very useful for investigating the individual constituents in various petroleum products but it frequently happens with shorter GLPC columns that one peak on the chromatogram represents three or more substances and identification of the substances in the separated fraction becomes difficult. With the 830 cm column used in the large unit this difficulty was reduced and identification simplified. Many of the constituents present in the alkylate shown in *Figure 5* were identified by the mass spectrometer. A similar

technique was applied to a sample of nonanes (see *Figure 9.*) Infra-red spectroscopy also had to be utilized in this case to identify positively the constituents separated from the mixture. Since it is generally necessary to

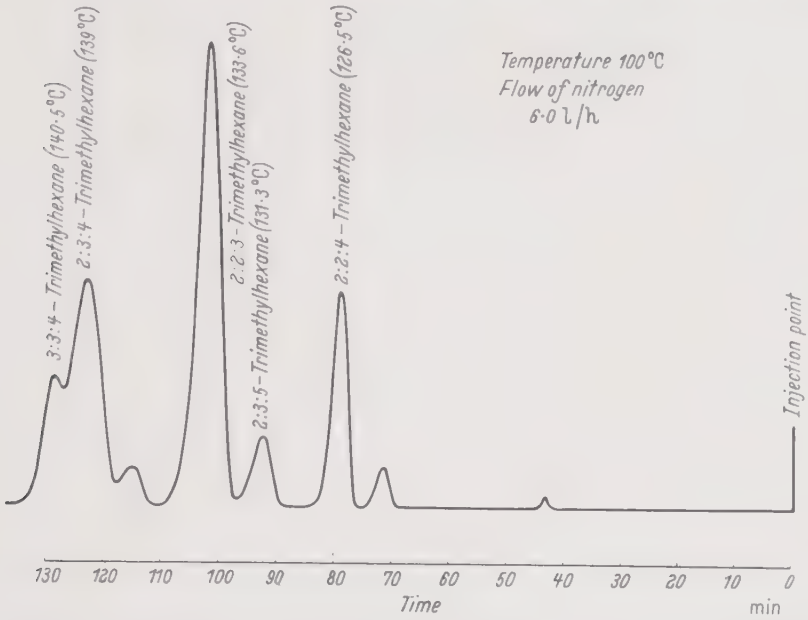

Figure 9. Nonanes 0·2 ml. *Large scale analytical GLPC unit.* 830 cm *column. Silicone fluid M.S. 550 stationary phase on 44–52 mesh Sterchamol brick*

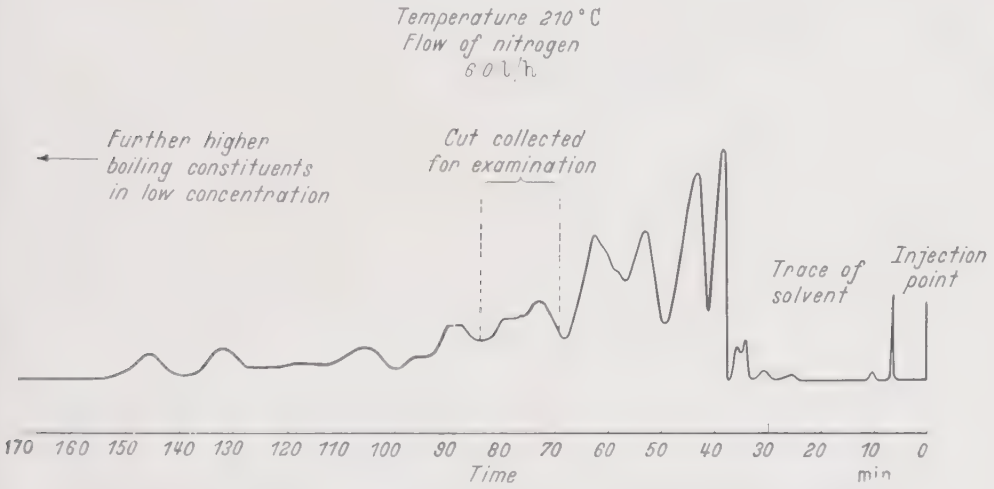
Temperature 210°C
Flow of nitrogen
6·0 l/h
Further higher boiling constituents in low concentration
Cut collected for examination
Trace of solvent
Injection point
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Time
min

Figure 10. Aromatics from petroleum fraction boiling range 170–260°C. 1·0 ml. *Large scale analytical GLPC unit.* 830 cm *column. Silicone fluid M.S. 550 stationary phase on 44–52 mesh Sterchamol brick*

separate larger amounts of sample for examination by infra-red spectroscopy than by mass spectroscopy, the large column is very useful in such circumstances.

For petroleum samples with boiling ranges above that of gasoline the separation of the individual compounds by GLPC is very difficult even when

specific classes of compounds, such as paraffins or aromatics, are being considered. Here GLPC becomes even more essentially complementary to such techniques as spectroscopy. Thus GLPC can be used to fractionate a gas oil or kerosine into narrow fractions which are analysed by other techniques and the large unit has been used in this field. An illustration of this was the investigation of a petroleum fraction boiling in the range 170–260 C. This

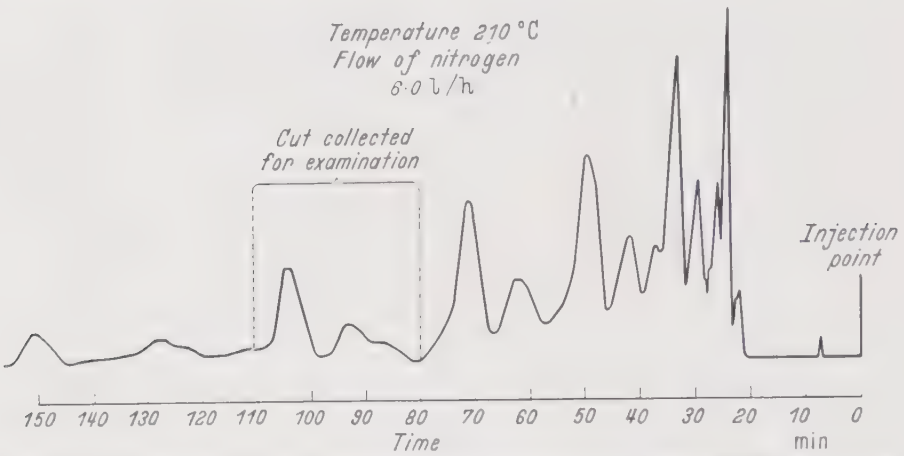

Figure 11. Paraffins (saturates) from petroleum fraction boiling range 170–260 C. 1·0 ml. *Large scale analytical GLPC unit.* 830 cm *column. Silicone fluid M.S. 550 stationary phase on 44–52 mesh Sterchamol brick*

was first split into aromatics (plus other polar compounds) and paraffins by liquid phase chromatography. The two fractions were then put through the large GLPC unit and a cut condensed from each. *Figures 10* and *11* show the chromatograms of the fractions and where the cuts were taken. These cuts were then analysed in a mass spectrometer and the results are shown in *Table II*. It will be seen that considerable information as to the constitution

Table II. Composition of Petroleum Cuts Separated by GLPC and Determined by Mass Spectroscopy

Aromatic cut separated from 170–260°C petroleum fraction		*Paraffinic cut separated from 170–260°C petroleum fraction*	
Major constituents		Major constituents	
Alkylbenzenes	C_{11} 20% v	iso*Paraffins*	C_{13}
	C_{12} 22% v		C_{14}
Indanes and tetralins	C_{10} 14% v	*Monocyclic naphthenes*	C_{13}
	C_{11} 27% v		C_{14}
	C_{12} 9% v	*Dicyclic naphthenes*	C_{12}
			C_{13}
Minor constituents		Minor constituents	
Alkylbenzenes	C_{10}		
Indanes and tetralins	C_9	*Monocyclic naphthenes*	C_{12}
		Dicyclic naphthenes	C_{14}
Naphthalene	C_{10}		

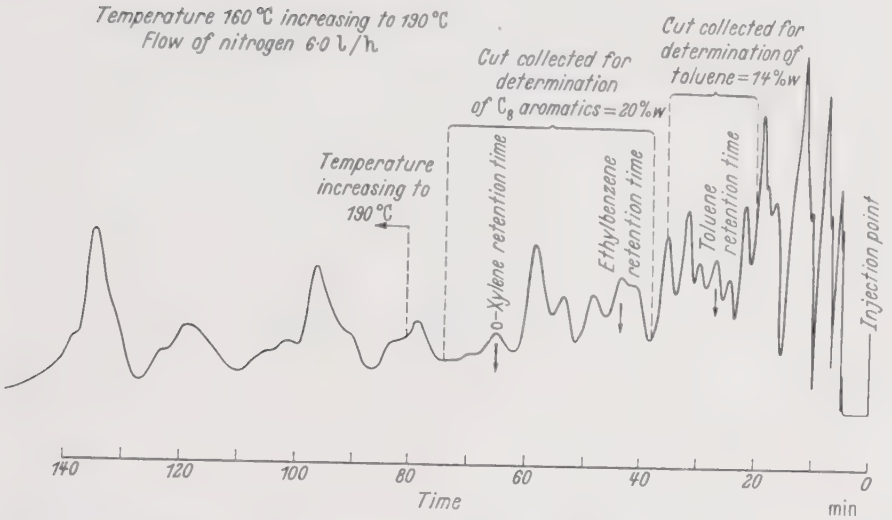

Figure 12. Aviation kerosine 3·0 ml. *Large scale analytical GLPC unit.* 830 cm *column. Silicone fluid M.S. 550 stationary phase on 44–52 mesh Sterchamol brick*

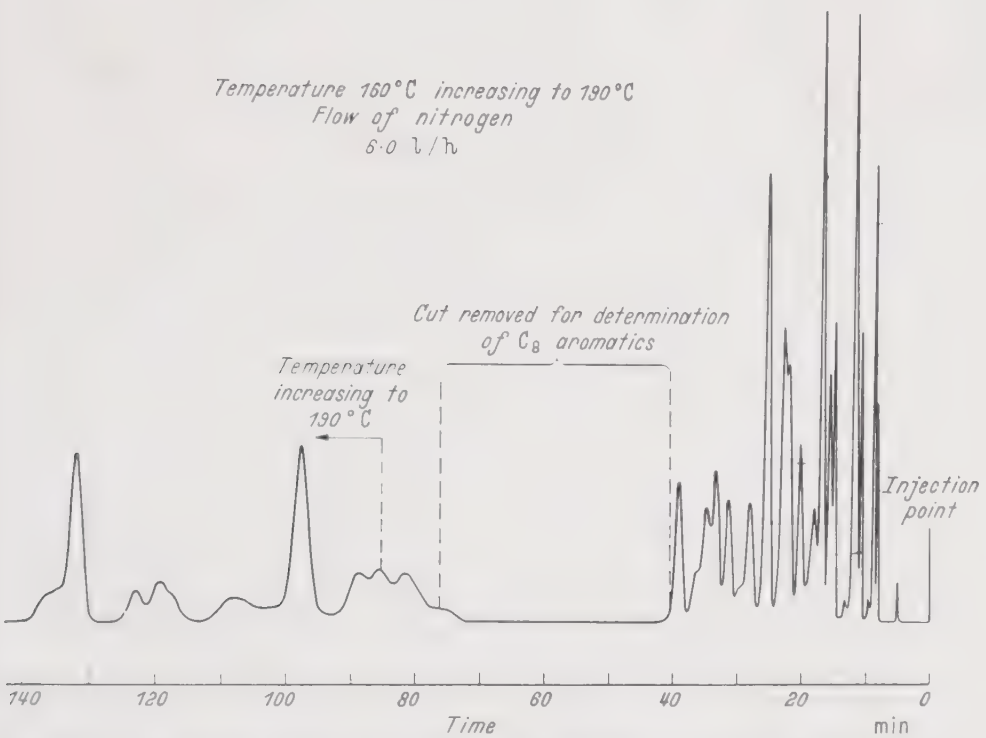

Figure 13. Aviation kerosine after removal of C_8 *aromatic cut.* 0·01 ml. *Large scale analytical GLPC unit.* 830 cm *column. Silicone fluid M.S. 550 stationary phase on 44–52 mesh Sterchamol brick*

of these cuts was obtained and by splitting up a kerosine or gas oil into a number of such fractions a very comprehensive analysis is possible. Unfortunately the mass spectrometer was unable to give quantitative results for the paraffinic fraction, since no method exists at the present time for the range of

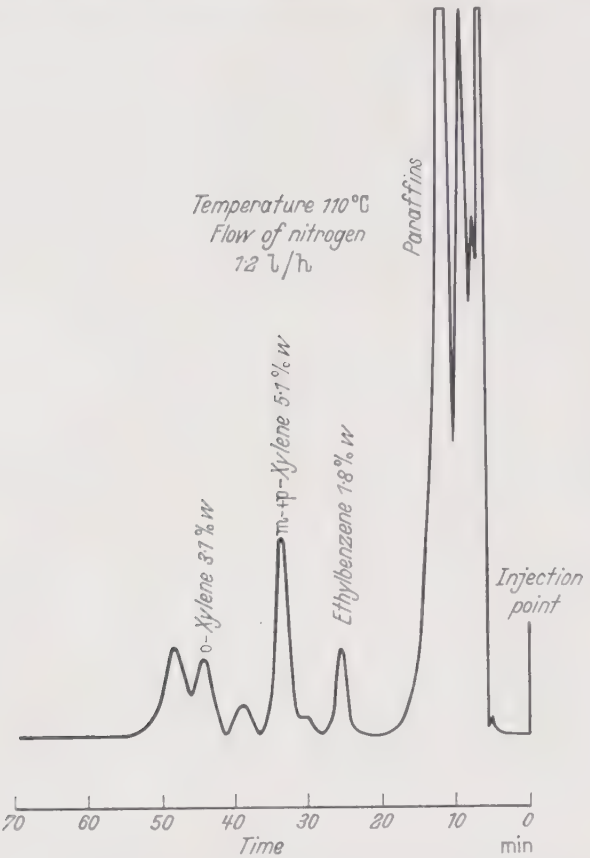

Figure 14. Cut containing C_8 *aromatics separated from an aviation kerosine by means of the large scale analytical GLPC unit.* 0·025 ml *sample size. Fluorene picrate stationary phase on Celite 545. Column* 184 cm

petroleum being considered. It is also interesting to note that definite peaks are obtained in the chromatograms of such complex mixtures and it seems that these may correspond to definite groups of compounds.

Similarly the large scale unit has been used to pre-fractionate a complex petroleum mixture to enable an accurate analysis of a particular compound or group of compounds to be obtained on the small GLPC units with a liquid stationary phase of different selectivity. As an example of this, the determination of the total C_8 aromatics in an aviation kerosine was carried out by first running the sample through the large scale unit and condensing out the fraction containing the particular group of compounds required. Here a 3 ml sample was used and an approximately $\frac{1}{2}$ ml fraction was isolated. A portion of this fraction was then run through a small analytical GLPC column containing a fluorene picrate stationary phase and the saturate constituents were grouped at the beginning of the chromatogram leaving the C_8 aromatics sufficiently separated to enable the amounts present to be estimated. Quantitative results were obtained from the corrected areas of the

peaks after addition of a known quantity of ethylbenzene as reference. *Figure 12* shows the trace for the whole kerosine when a 3·0 ml sample was used. *Figure 13* shows the trace for the kerosine after removal of the fraction containing the C_8 aromatics. *Figure 14* shows the trace for the separated fraction on a fluorene picrate column. The amount of C_8 aromatics present in the original kerosine was shown to be 2·0 per cent. A similar technique was used to determine the toluene content. The trace for this particular fraction on a fluorene picrate column is shown in *Figure 15*. The amount of toluene

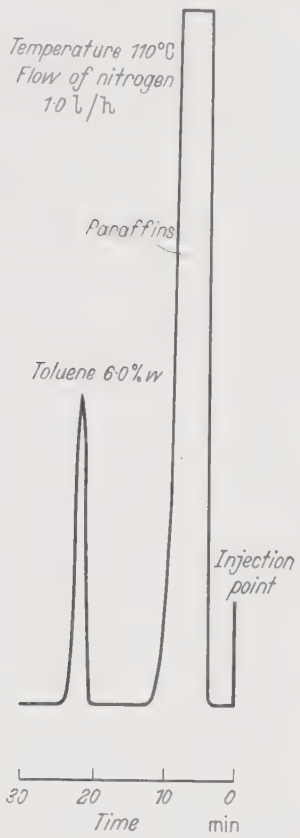

Figure 15. Cut containing toluene separated from an aviation kerosine by means of the large scale analytical GLPC unit. 0·025 ml *sample size. Fluorene picrate stationary phase on Celite 545. Column* 184 cm

present in the original kerosine was shown to be 0·8 per cent. There are variations of this procedure which can be usefully applied to fractionate petroleum and other complex mixtures. The large scale unit can first fractionate a complex mixture mainly according to boiling point, and then the fractions can be type separated on the small columns using selective liquid stationary phases as described above. Alternatively, the large unit can be used to achieve a type separation with a selective liquid stationary phase and the type fractions can then be separated on the small columns with liquid stationary phases particularly suited to the groups of compounds obtained. These procedures frequently make it possible to dispense with the time-consuming liquid solid adsorption methods for type separation of mixtures

and can be utilized to determine substances down to concentrations of a few parts per million or even lower in complex mixtures.

The use of hydrogen as the carrier gas enables a considerably greater sensitivity to be obtained with thermal conductivity measurements and this can be utilized to detect trace impurities directly. As an example it was found possible to detect 50 p.p.m. of toluene in a sample of *n*-heptane using a $\frac{1}{2}$ ml sample (see *Figure 16*). Thus, with this technique and even bigger

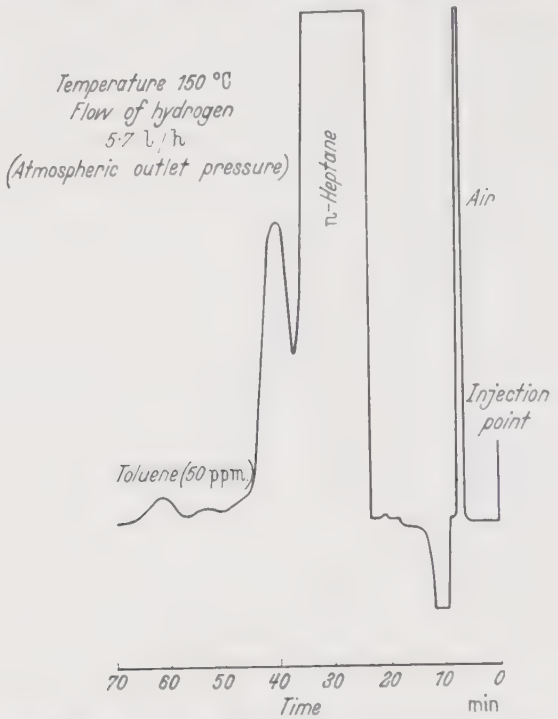

Figure 16. n-*Heptane.* 0·50 ml. *Large scale analytical GLPC unit.* 830 cm *column.* ***Silicone fluid M.S. 550 stationary phase on 44–52 mesh Sterchamol brick***

sample sizes, detection and estimation of a few parts per million of impurities present few difficulties with simple mixtures. In many cases the direct detection of such minor impurities may be possible on the small analytical columns.

Finally, the large column is proving extremely useful for preparing millilitre quantities of pure hydrocarbons in the gasoline range for experimental work and for calibration purposes in spectroscopy and GLPC. For some purposes columns of increased diameter and even greater length will prove useful and these can conveniently be incorporated in the present furnace unit. It seems from the present results that the separating power of such columns will increase in proportion to the length and further increases in diameter may be possible without any loss in efficiency, provided a suitable liquid phase support is used.

The author wishes to thank the Directors of 'Shell' Research Limited for permission to publish this paper, also those members of the Thornton staff, particularly Messrs E. R. Adlard, P. J. Moore, A. Quayle and W. A. L. Watt, ***who have taken part in the work described.***

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DISCUSSION

D. Ambrose: Recently Mr Collinson and I published a letter in *Nature* about the use of gas chromatography as a preparative method. We published it in that form because at that time it did not appear that we had enough material to offer as a full length paper to this symposium, but in view of several points which have been made by other speakers I think we can usefully contribute to the discussion and this seems a suitable point at which to interpolate it as we are trying to work on a scale similar to that of Mr Whitham.

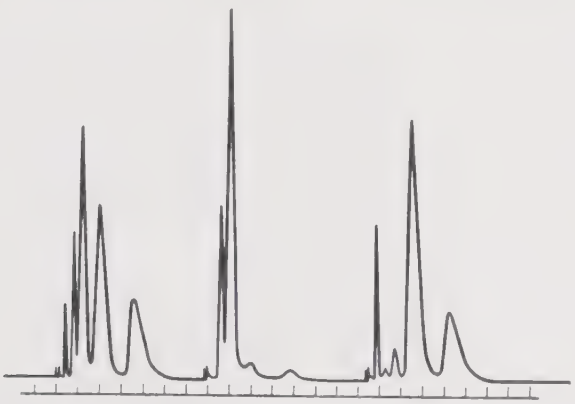

Figure 17. Separation of C_4 mixture, using silver nitrate in glycol column

If I may summarize our method, we have been trying to purify C_4-hydrocarbon gases on columns operating at room temperature under conditions in which the separations are complete in about twenty minutes, by the automatic repetition of the cycle of injection and collection of the cycle of wanted material. The addition of the sample, which is under pressure, is simply achieved by opening a solenoid-operated valve, and provided the retention times remain constant, it is possible to control both this and the second solenoid-operated valve in the outlet by means of a clock, so as to divide the sample into two fractions of pre-determined concentration. Once set going the apparatus runs indefinitely with at present a throughput of about three grammes an hour and requires attention only once a day.

Figure 17 shows results which we obtained in initial trial runs on a C_4 fuel gas. There are three traces of the three separate mixtures. The one on the left shows five components, which was the original feed material, and the other two show the composition of the fractions into which it was resolved. The apparatus had been set to remove peaks 2 and 3 which you will see are present and much in evidence in the middle trace. Peak 4, of course, appears because the separation is not complete between 3 and 4. Peak 5 appears where one would not expect it, through slight maladjustment of the cycle, and in fact the point of injection of the next sample occurred in the tail of peak 5 before it had been completely isolated.

Since this work was done we have been working with mixtures more suitable for the extraction of a single pure substance and are now developing it for use with normally liquid materials.

From our own experience with this I should like to discuss three points which have been raised previously: the collection of the sample, the drying-out of the column, and the comparison of plate values for chromatograph and distillation columns.

The development of the method on the system shown in the diagram proved straightforward in its chromatographic aspects, and the fear that we might have difficulty in maintaining the exact constancy of pattern in the selected peaks (when a more complicated control involving the detector as well as the clock would be required) proved groundless. The only difficulty was that after passing some 50-100 g of raw material through the apparatus our collecting traps, which were immersed in solid carbon dioxide, proved to be empty! We used solid carbon dioxide for economy and because we wished them to last overnight without any attention. The biggest problem to be solved in fact was the recovery of the separated material which is of course, as has already been mentioned, present in only a relatively low concentration in the carrier gas. We succeeded for these C_4 gases by filling the traps with activated alumina. Glass beads proved inadequate, so presumably the absorptive power of the alumina was required in addition to its action as a baffle and heat-transfer agent; an active charcoal, on the other hand, removed the eluted material from the gas stream and held it too tenaciously to be useful. With the alumina we get substantially complete removal from the carrier, and the hydrocarbon can be recovered by simply reducing the pressure and allowing it to distil into another empty trap immersed in liquid nitrogen.

We have consequently concluded that for our purpose an empty trap is useless and it is interesting to compare our and other experience in this field with attempts to dry air by refrigeration, a process of interest in the industrial separation of gases by distillation. It is in fact difficult to lower the water content of a stream of gas to its theoretical limit by cooling. Some members of the National Physics Laboratory some years ago found that a succession of three traps immersed in liquid nitrogen was necessary for the reason given by Mr van der Craats yesterday—namely that the water was precipitated as minute crystals which were carried forward in the stream of gas. They concluded that it was essential to ensure a sufficient rise of temperature between traps for the ice crystals thus carried on to re-evaporate.

When we turned from our trial mixture to do a serious purification of *iso*butene, using tri*iso*butene as the stationary phase, our preliminary experiments seemed to have deceived us since the retention times were constantly varying and we considered a number of possible causes which might have originated in the changing temperature of the laboratory during 24 hours. After finding that the difficulty was not overcome by making the temperature of the column constant by packing it in ice, the pre-saturation of the carrier gas with the stationary phase was found to be the complete answer. In fact the variations had been all in one direction—that of decreasing retention time—and when the saturator was inserted at room temperature with the column still in ice the retention times gradually lengthened and returned to their original values. They then remained constant for the duration of the experiment although doubtless had we continued long enough using the two different temperatures we might have found them lengthening further as the column became overloaded with tri*iso*butene. With our earlier trial mixture, where the operative agent was silver nitrate, one might expect any evaporation to have less effect.

In conclusion I should like to take up the question of the significance of the term 'plate value' as used for distillation and chromatograph columns. In this I am somewhat at variance with my colleague, Dr Herington, in that I think the data he gave are too pessimistic with regard to the performance of the chromatograph

column in view of the way in which it is used in practice. Where I think we are in complete agreement is that despite the formal identity of definition of the HETP as the basis for the theories of both processes the resultant plate values of the given column cannot be compared in any direct way: and there is no need for those brought up on distillation to be too overcome by the staggering number of plates in the chromatograph column. If I understood him correctly his value of 500,000 plates implied a separation in which there was only an overlap of 0·1 per cent.

This means, however, that in our apparatus we could obtain a yield of perhaps 80 per cent of the material in a purity of 99·99 per cent since we can reject the entire part of the peak where there is overlap and such a purity would demand a doubling of the plate value of a distillation column with consequent reduction in throughput. In fact for the mixture of some substances usually handled by fractional distillation the raising of the concentration from 50 to 90 or 95 per cent presents no particularly difficult problem. I suggest that our technique will offer opportunities for easily achieving high purities from the 95 per cent materials which are very difficult for distillation. I am of course here considering this from the laboratory point of view and not entering into the question of any energy involved from the chemical and technical engineering aspect of it.

A. KLINKENBERG: I noted both from Dr Ambrose's paper and from Mr van der Craats's contribution to the discussion that there is a problem of how to prevent fog formation or entrainment of solidified solute during the cooling of a gas–vapour mixture.

The mechanism is one of simultaneous flow of heat and mass (i.e. solute) from the core to the wall of the tube. These processes are described by the same equations and there enters in each of these equations a single physical property, viz.:

in the flow of heat: the thermal diffusivity a
in the flow of mass: the diffusion constant D

Let us examine first the case where a and D are equal, i.e.

$$a/D = Le = 1 \quad (Le = \text{'Lewis group'})$$

The states of the conceivable gas–vapour mixtures may be indicated in a 'solute content versus temperature diagram', as follows:

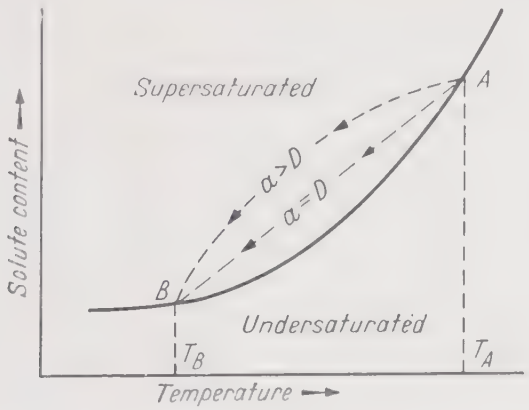

Figure 18

In such a diagram, the vapour pressure curve separates the regions of the unsaturated and supersaturated states.

If saturated vapour A is cooled from T_A to T_B, in the case of $a = D$ the straight line AB will be followed, and there will be produced a moderate degree of supersaturation with some possibility of fog formation.

In the case of a · D the gas will lose its heat much faster than the solute. Fog is bound to form.

This behaviour is well demonstrated in experiments by Hilz[7], interpreted later on the above lines by Hausen[8].

The mixtures cooled were:

(*1*) Nitrogen–water
(*2*) Hydrogen–water
(*3*) Nitrogen–benzene.

In case *1* the diffusing vapour and the carrier gas have similar molecular weights. This leads to $Le \fallingdotseq 1$. When passing the moist nitrogen through a tube cooled to −78°C, the issuing gas was clear.

In cases *2* and *3*, D was much lower than a, Le · 1, and 'snow' was produced in the issuing gas.

A similar case is encountered in the commercial production of sulphur by partial combustion of sulphuretted hydrogen, the sulphur vapour having a molecular weight of 256. Reference is made to Johnstone and co-workers[9]. Considerable amounts of persistent fog are indeed formed in this process during cooling.

Remedies all meant to avoid the most highly supersaturated region are:

(*i*) Cooling in several steps (going from A to B by several short chords)
(*ii*) Starting with a superheated vapour (to the right of A)
(*iii*) Ending with an undersaturated vapour (below B). This is realized if the cooling is carried out in the presence of an adsorbent or absorbent
(*iv*) Supplying extra heat while the gas is being cooled, e.g. by means of an electrically heated wire along the axis of the tube.

This proposal, made in the chemical engineering field by Colburn and Edison[10], has also been applied by Martin[11].

(*v*) Furthermore turbulent flow is preferable to laminar flow. This point, discussed by Johnstone, may be outside the sphere of the chromatographer's interest.

Mr van der Craats's suggestion of repeated cooling and heating in a zig-zag tube, partially immersed in the coolant, could be considered an example of method *ii*.

It should be interesting to know if fogs are indeed most frequently observed for the highest molecular weight vapours in the lowest molecular weight carrier gases.

Discussion References

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18

SOME PROBLEMS ENCOUNTERED WITH THE APPLICATION OF VAPOUR PHASE CHROMATOGRAPHY TO KINETIC STUDIES

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Vapour phase chromatography, with the assistance of mass spectrometry, has been adapted to the special problem of investigating gas phase reactions. Provisions for the recovery of vapour phase chromatographic fractions required changes in the arrangement of the detector.

Since high column temperatures produced objectionable quantities of water and some other higher boiling point materials in the recovered fractions, a column with a low operating temperature was employed. Expendable traps with low hold-up volume and sintered glass packing were developed for the special problems encountered in the recovery of very small fractions. Improvements in column performance and increase in elution rate were made by using programmed heating of the column during the analysis. To work with deuterated hydrocarbons emphasis is placed on the necessity of using vapour phase chromatography followed by mass spectrometer analysis of the recovered fractions.

In recent years mass spectrometry has been employed extensively in the study of gas phase reactions, and for some purposes it is the only tool capable of meeting analytical requirements. The analysis of some mixtures can become quite complicated when an undetermined number of unknown compounds is present. If the identities of components are known, quantitative mass spectral analysis is possible. When there is a wide distribution of percentage concentrations among the compounds present the analysis is difficult and less accurate than when there are only large concentrations. In the field of gas phase kinetics it is necessary to analyse samples of this very nature. Usually a reaction is carried to only a few per cent conversion, producing an unknown variety of reaction products which must be accurately analysed in the presence of a large excess of unreacted material. Experimental conditions often restrict the sample size of the original reaction mixture so that the amount of each product to be analysed is of the order of a few microgrammes. Until recently the mass spectrometer has been the only instrument capable of dealing with such minute quantities[1]. While good analytical data are necessary in order to understand a reaction, frequently detailed knowledge of the reaction mechanism is best obtained by tagging the reactants with deuterium. The introduction of deuterium increases the mass spectrometer analytical difficulties, so that only very simple systems can be treated with good understanding. These difficulties arise for two reasons.

First, the mixtures are often so complex that qualitative analysis by mass spectrometry is very difficult, if not impossible. Secondly, even if the qualitative analysis is known, the pure compounds whose spectra are required for quantitative analysis are frequently unavailable.

With vapour phase chromatography (VPC) these mixtures can be resolved into fractions containing only one or two compounds. If these fractions are recovered and analysed separately by mass spectrometry, usually the desired information can be obtained. Since it is not always possible to separate a mixture completely by VPC without modifications in the apparatus, it is

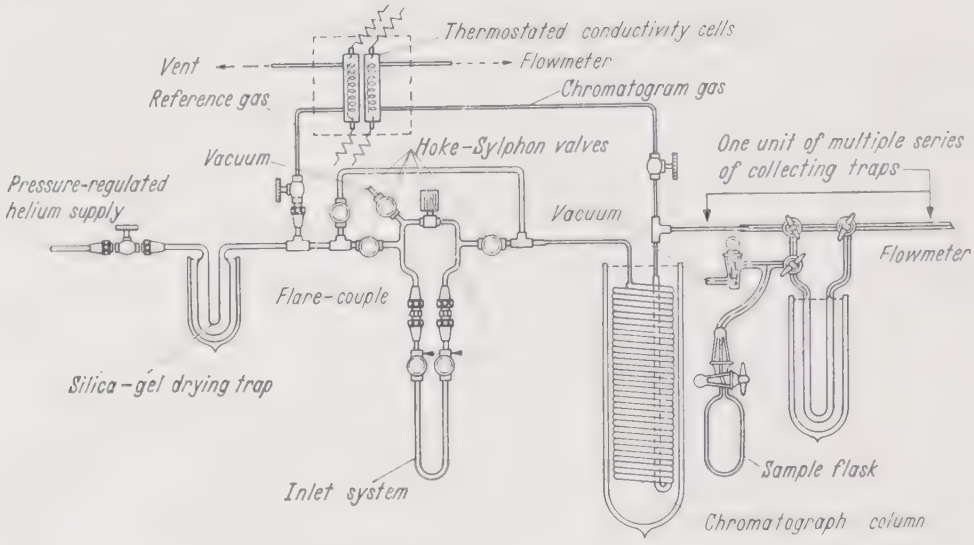

Figure 1. Schematic arrangement of the apparatus

sometimes expedient to complete the analysis of mixed fractions by mass spectrometry. Also, since VPC cannot be used for the location of deuterium in a molecule the VPC apparatus should be provided with means for recovering the fractions as they emerge from the column.

The recovery of VPC fractions especially with very small samples presents several difficulties requiring techniques which will be outlined here.

1. Apparatus and Procedure

1.0. *Detector arrangement*

In this work a conventional heated filament detector and bridge circuit was used. It was found that the passage of some thermally unstable materials such as methyl acetylene over the hot wire produced undesirable polymerization reactions. This introduced impurities in the recovered fractions. This difficulty was overcome by diverting only a small portion of the exit stream from the column through the detector and letting the main portion go directly to the collecting traps. *Figure 1* is a schematic arrangement of the apparatus. A small amount of pure helium (carrier gas) was similarly diverted through the reference side of the detector. Because programmed temperature rise was applied to the column during runs the helium flow rate through the column varied as a function of column temperature due to the change in viscosity of helium. This produced a slight gradual change in the pressure of

the system and also in the measuring side of the detector, and resulted in a serious drift in the bridge output at high sensitivities. The drift was minimized by coupling the exits from both the measuring and the reference sides of the detector through a T to a sintered glass type restriction (not shown in the figure). This arrangement assured that both sides of the detector remained at the same pressure, thus largely compensating the pressure drift effect. The flow rate through the detector was set at approximately 5–10 per cent of the total flow through the system by means of an indicator bubbler (also not shown). The assembly was thermostatted at 30 C. Since thermal conductivity detectors respond primarily to changes in concentration or pressure and very little to flow rate changes, this arrangement still permits good quantitative work.

1.1. *Column assembly*

Figure 2 is a cut away drawing of the column and the arrangement used for gradually increasing column temperature during a run. The entire assembly was placed in a close-fitting Dewar flask to prevent heat exchange with surroundings. In operation the assembly was cooled to the desired temperature with refrigerants. Very low temperatures (−195°C) could be obtained

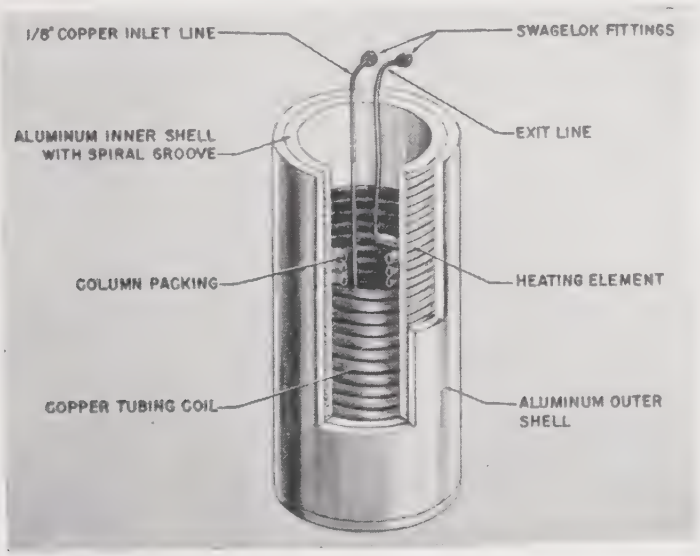

Figure 2. Cut away drawing of arrangement for varying column temperature over a wide range

by pouring liquid nitrogen into the central opening. Desired heating rates were achieved by applying the proper voltage to the embedded heating element. At a given voltage the rate of temperature rise depended mostly upon the total heat capacity of the system since heat exchange with surroundings was held to a minimum. In practice the rate of temperature rise varied almost linearly with time and was quite reproducible on successive runs. At maximum voltage the temperature could be changed from −195 C to over +300°C within one hour.

1.2. *Trap arrangement for recovery of average sized fractions*

A series of 12 U-tube traps was arranged with stopcocks as shown in *Figure 1*, so that the main portion of the exit gas stream from the column could be diverted at will through any of the traps or by-passed around them. As many as 12 fractions could be recovered by passing the exit gas from the column through the desired trap, at liquid nitrogen temperature, during the emergence time for the particular fraction being recovered, then changing traps for each subsequent fraction. Provision was made for pumping off excess helium and distilling the material into a mass spectrometer sample flask as shown in *Figure 1*.

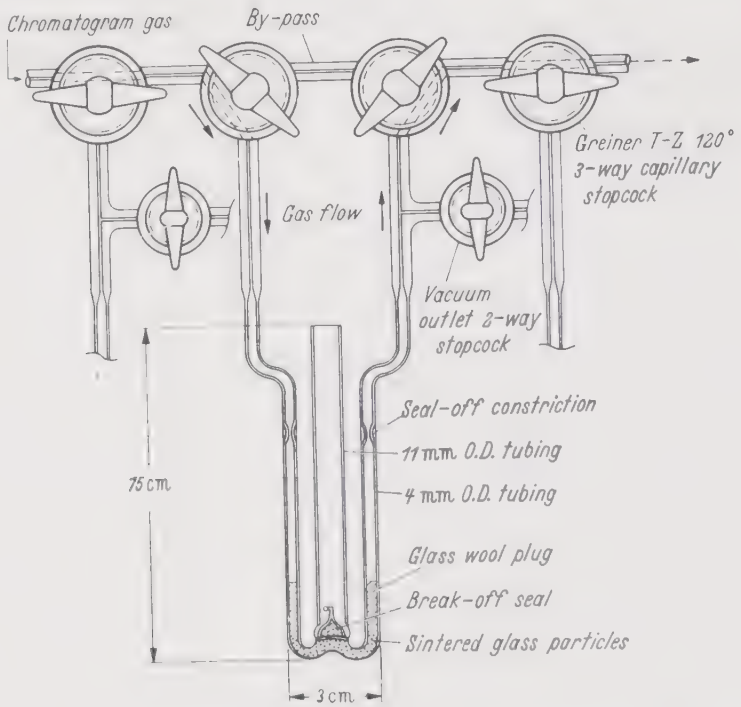

Figure 3. Trap arrangement for recovery of extremely small fractions

1.3. *Trap arrangement for recovery of extremely small fractions*

The recovery system described above (1.2) was quite suitable for sample sizes of a few milligrammes or larger, and is recommended for general usage since it does not involve difficult or laborious techniques. However, the system is unsuited for the recovery of extremely small fractions. Serious losses are encountered due to insufficient entrainment of the condensable material even at liquid nitrogen temperature. If the U-tube is packed with adsorbent to improve entrainment it is difficult to transfer the sample to the mass spectrometer flask because of the relatively large volumes and surface areas involved. Also, large amounts of background contamination are encountered.

Figure 3 illustrates the schematic arrangement which was successfully used to recover and analyse fractions weighing less than 30 microgrammes. Essentially the method consists of using much smaller expendable U-tubes packed with thoroughly baked out sintered Pyrex glass entrainment particles.

The U-tubes are arranged so that they can be evacuated and sealed off from the manifold after fractions are captured. They are also provided with break-seal entries so that their contents can be introduced into the mass spectrometer. For low boiling compounds such as methane and carbon monoxide, activated charcoal was substituted for the sintered glass.

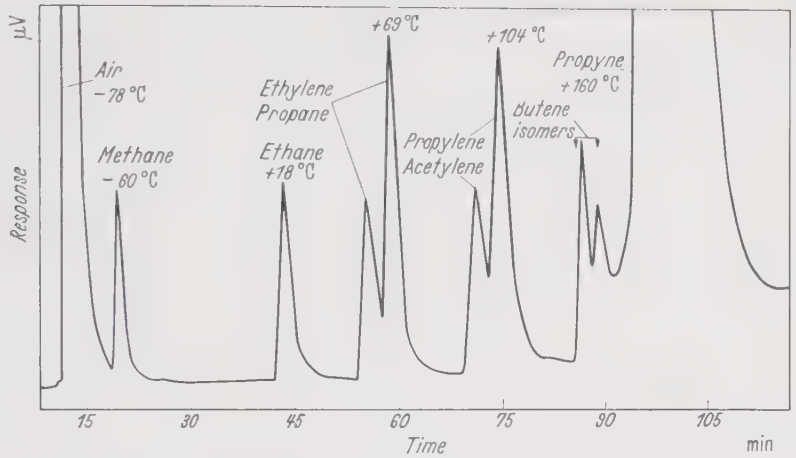

Figure 4. Separation of hydrocarbons C_1–C_4 on porous Vycor with a large excess of methylacetylene. Column length, 15 ft

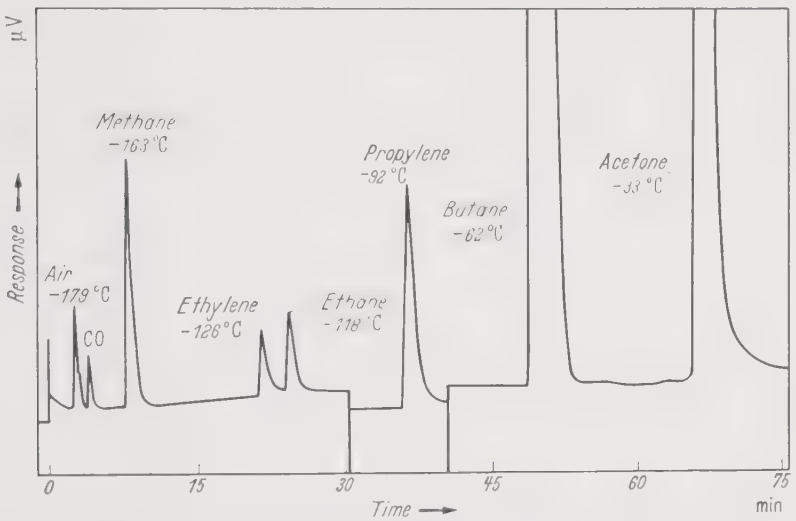

Figure 5. Typical analysis of products produced by photolysis of mixture of acetone and butane using a 6 ft *column of* 1·5 per cent *Octoil-S on Pelletex*

1.4. *Programming column temperature*

Griffiths, James and Phillips[2] employed the technique of gradually increasing column temperature during elution to give both improved separation and uniformly well shaped peaks for each compound as the result of reduced tailing. Since then little attention has been given to this important technique. Nearly all subsequent work has been done with constant temperature control on the column, with the result that low boiling compounds tend to emerge rapidly with extremely sharp elution peaks and as higher boiling point materials

emerge their pattern spreads out accordingly. This makes it difficult to measure peak areas for quantitative work. Furthermore, the long times required for eluting the high boiling materials are objectionable and the sensitivity limitations of the detector necessitate rather large samples when severe tailing or broadening is encountered. Although these objections can largely be overcome by making more than one run at different temperatures, it requires more than one sample and considerable repetition of effort to obtain a complete analysis. Patton, Lewis and Kaye[3] recommend that area measurements on chromatogram peaks be made by multiplying the height of the peak times the peak width at one half the peak height. This method is as accurate as, and more convenient, than a planimeter, but it assumes a triangular shape for the peak. In practice it seems advisable to choose conditions giving a good triangular elution pattern for as many of the fractions as possible. With programmed heating this can be accomplished readily. *Figures 4* and *5* are typical chromatograms using this technique.

1.5. *Temperature range*

The appearance temperature for a given fraction at relatively high heating rates depends largely upon the choice of sorbent used in the column and to a much smaller extent, upon the column dimensions, carrier gas flow rate, and rate of heating. With solid adsorbents, such as silica gel and activated charcoal, it is usually necessary to operate the column over a very wide temperature range in order to handle a reasonable spread of boiling points. Rather high temperatures are required for molecules C_5 and higher with the danger of pyrolysis reactions occurring on the column. This is especially true with olefins on silica gel or Vycor glass. *Figure 4* represents the separation of a number of saturated and unsaturated compounds from C_1–C_4 on a 15-foot column of unfired Vycor glass particles (20–80 mesh), which is a very porous material and somewhat less active than silica gel. Propylene required about 104°C before appearing.

It was found that water invariably comes off the columns at moderately high temperatures and its rate of elution increases rapidly as the temperature continues upward. This produces base line drift as shown in *Figure 4*. The amount of drift depends on previous bake-out conditions of the column but can never be completely eliminated with a silica gel type adsorbent at higher temperatures. Recovery of fractions under such conditions leads to very serious contamination with water. It is therefore desirable to choose a column which will handle the materials of interest below the appearance range of water or choose a column which can be dried easily. These conditions are met by a liquid-modified activated charcoal adsorbent* which has been used to study the initial reaction products produced by the photolysis and pyrolysis of acetone–butane mixtures. This column is a slight modification of the one described by Eggertsen, Knight and Groenings* which they used for separation of all the isomers of hexane at +40°C. The column used in this work and for the separation shown in *Figure 5* was a 6-foot column of 20–40 mesh

* The authors wish to express their appreciation to Shell Development Company, Emeryville, California, for permission to refer to liquid-modified solid adsorbents which are described in a forthcoming publication 'Gas Chromatography of Hydrocarbons – Resolution of C_5 and C_6 Saturates', by F. T. Eggertsen, H. S. Knight and S. Groenings.

Pelletex† with 1·5 per cent Octoil-S. Propylene appears at −92 C and no water appears until about 0 C. Unlike most other columns, water is virtually completely driven off between 0 and 20 C and it can therefore be eliminated by a brief passage of carrier gas at room temperature before chilling the column for an analysis. When longer columns of this material were tried, the olefins showed marked increase in tailing and prevented the good separation between ethylene and ethane (*Figure 5*).

With gas–liquid partition columns it is necessary to use an initial column temperature which is higher than the freezing point of the stationary phase. If lower temperatures are used, the lower boiling point materials, because of greatly reduced solubility in the frozen stationary phase, will pass through the column rapidly with little separation. If the column temperature is too high, there is also poor separation because of reduced solubility in the stationary liquid phase. With low molecular weight gases optimum separation is obtained by starting near the freezing point of the stationary phase.

The appearance temperature of compounds on a particular column is independent of starting temperature, provided that the starting temperature is lower than the appearance temperature, and that rather high rates of temperature rise are employed. If the column were started at a temperature higher than this characteristic elution temperature these affected compounds appeared rapidly and crowded together with sharp peaks, but the remainder appeared at the same temperatures that were observed when much lower starting temperatures were employed. Apparently there is a very narrow temperature range required to allow materials to migrate along the adsorbent bed at reasonable rates which result in good separation. If reliance is to be placed on increase in column length for better resolution, then heating rates must necessarily be slower, so that the migration time for each compound through the bed will occur within the narrow temperature range where there is good separation for that compound. A more rapid heating rate at a given flow rate will permit only part of the column to separate effectively.

1.6. *Sample recovery*

The apparatus for recovering samples is described under 1.2. In order to obtain pure fractions, however, it was found that thermally unstable material could not be passed through the detector (1.0), and that water background from the column must be eliminated. The column temperature must be kept low enough to avoid undesirable reactions on the column (1.4, 1.5). With extremely small samples it was also found necessary to pump out the manifold to a pressure of a few microns of mercury shortly before usage to remove adsorbed material accumulated in the lines and possibly in the stopcock greases. If all these steps were taken it was possible to analyse and recover fractions of 30 microgrammes or less with acceptably low background contamination. Most of the peaks on scale in *Figure 5* represent samples of this order of magnitude. For instance, the carbon monoxide fraction is 17 microgrammes.

The offset in the base line (*Figure 5*) just prior to and following the propylene fraction is due to the slight change in the system pressure caused by diverting

† Pelletized carbon black manufactured by Godfrey L. Cabot, Inc., Boston, Mass.

the stream through a trap (*Figure 3*) for the recovery of this fraction, then by-passing the stream again when elution of the fraction was completed. This change in base line has no effect on area measurements, provided the change occurs only in regions where the base line is stable. If two or more fractions do not completely separate it is advisable to recover all the overlapping fractions in one trap and complete the analysis by mass spectrometry. This technique of recovering groups of fractions can make the mass spectrometer analysis of difficult mixtures much easier and does not require complete separation of all the fractions. With deuterated unknowns, however, it is best to have complete separation of all fractions, since each fraction may contain a number of partially deuterated homologues.

1.7. *Analysis of mixtures with trace constituents*

Figures 4 and *5* are analyses made on mixtures having very large concentrations of one or two components with trace amounts of the materials which are those with peaks that are still on scale. These are typical analytical problems handled by VPC in this laboratory. Sometimes it is necessary to measure the amounts of these materials which lie beyond the range of the recorder in order to estimate the degree of completion of a reaction. Three methods are available. The bridge sensitivity can be reduced for the large materials, or extended range and multiple sensitivity recorders can be employed. A third method which has been employed successfully is to add a trace of inert gas to the original reaction blend and determine its concentration relative to the larger components accurately with an independent method. In the subsequent VPC analysis of reactions using this blend, the original sample size can be determined from the quantitative determination of the inert gas additive. The only requirement from the standpoint of the analysis is that the inert gas shall appear in a region free of other fractions. In the study of acetone–butane reactions of which *Figure 5* is an analysis made on photolysis products of this mixture, xenon was employed in this manner. Xenon will appear just ahead of the ethane fraction under the conditions of this analysis. Its determination fixes the initial amounts of butane and acetone which are far off scale.

1.8. *Further applications*

Recovery of VPC fractions makes the method suitable for the preparation of pure compounds for other research problems[1]. It can be used to prepare standards (ordinarily not available) for mass spectrometry or for other analytical work. In fact, the mass spectrometer analysis of recovered fractions from a reaction automatically furnishes standard cracking patterns for this material, provided it is a single compound with sufficiently low background contamination.

References

[1] Callear, A. B. and Cvetanovic, R. J. *Canad. J. Chem.* **33**, 1256, 1955
[2] Griffiths, J., James, D. and Phillips, C. *Analyst* **77**, 897, 1952
[3] Patton, H. W., Lewis, J. S. and Kaye, W. I. *Analyt. Chem.* **27**, 170, 1955
[4] McNesby, J. R., Drew, C. M. and Gordon, A. S. *J. phys. Chem.* **59**, 988, 1955

DISCUSSION

K. O. Kutschke: I would like to ask Mr Drew about the sensitivity of his device. I believe I know the answer, but he was speaking of using rather smallish quantities and had, as far as I could see from the diagrams, merely one thermal conductivity cell. I want to ask whether it is correct to use a d.c. amplifier preceding the recorder?

C. M. Drew: You are quite correct. We omitted such details from the text because they are now generally recognized arrangements. Actually we used a Leeds Northrup d.c. linear amplifier ahead of the recorder.

19

VAPOUR PHASE CHROMATOGRAPHY AT HIGH TEMPERATURES

J. G. KEPPLER, G. DIJKSTRA and J. A. SCHOLS
Unilever Research Laboratory, Vlaardingen, The Netherlands

A description is given of an apparatus for vapour phase chromatography designed for use at temperatures up to 300 C to facilitate analysis of samples of microgramme size as well as collection of the fractions separated.

Heat conductivity cells are employed as detection elements. Two types are used: metal cells which can withstand temperatures up to 250 C and glass cells for temperatures up to 300°C.

The influence of cell current and cell temperature on the sensitivity of the katharometers are discussed.

The performance of immobile phases tested for use at these temperatures is compared.

Some of the substances detected show a peak inversion at high temperatures and the origin of this phenomenon is discussed.

EXPERIENCE in the analysis, by gas–liquid partition chromatography, of substances with high boiling points as, for example, fatty acid methyl esters and fatty alcohols, has clearly shown the necessity of working at temperatures in the 150–270°C range[1,2]. This, however, presented special problems in connection with methods and apparatus, namely:

(*1*) The temperature-control equipment had to be capable of maintaining the desired temperatures—within the 150–270°C range—accurate to within ±1C°.

Detection methods had to be chosen or evolved, which were adaptable to these high temperatures.

(*2*) The detector had to be suitable for such high working temperatures, and two types were carefully considered:

(*a*) Metal katharometers, for use at a maximum temperature of 250°C.

(*b*) All-glass katharometers constructed to withstand safely temperatures up to 300°C.

(*3*) With such high column temperatures it was essential that the stationary phase should be completely inert and immovable.

In addition the following points were carefully borne in mind:

(*4*) For accurate determination of small amounts of substance (100 μg down to 0·5 μg) the thermal conductivity cells had to possess the utmost sensitivity.

(*5*) As a result of degradation—brought about by the high temperatures—certain substances exhibit typical recorder images on passing through the detector.

(*6*) Means must be available for the individual collection of each of the

separated substances, in cold traps at atmospheric pressure, where this is considered desirable.

1. Heating System

Figure 1 depicts the type of metal apparatus employed in this laboratory for gas–liquid chromatography. Both the metal *detection* cell and the stainless steel *column* are electrically heated, the latter by means of resistance wire.

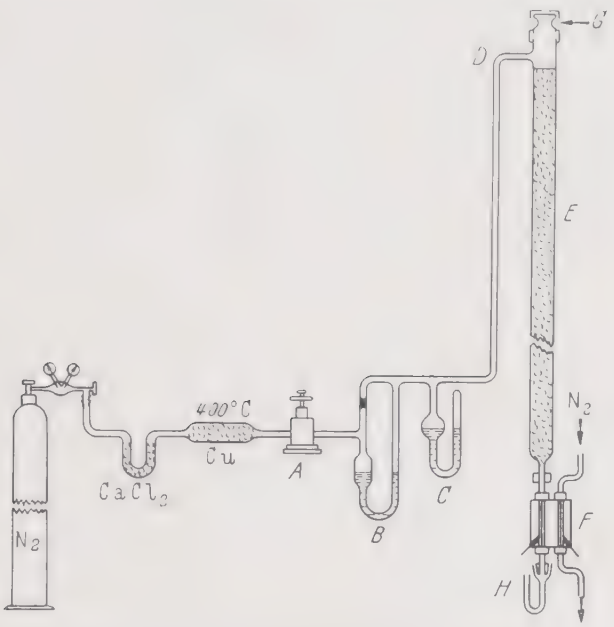

Figure 1. General arrangement of apparatus

The temperature can be kept constant to within $\pm 1C$, in the 200–270°C range, which, for analytical purposes, is sufficiently accurate.

The simplest way to heat the *katharometer* is with heating tape.

An important advantage of the all-electrical heating is that it enables the current lead-in wires of the Wheatstone bridge in the detector cell to be much more easily installed than when the apparatus is heated by a vapour or a liquid-bath. The temperature is regulated and controlled by means of a variable transformer. Bimetal switches of the Simmerstat type cannot be used on account of induction effects which occur when switching on and off.

2. Thermal Conductivity Cells for Use at High Temperatures

When analysing substances with high boiling points it is necessary for the detection-cell channels to be at such a temperature that none of the substances involved can condense. Should this happen, trailing effects occur which either interfere with or completely prevent detection.

The katharometers (thermal conductivity cells) shown in *Table 1* were employed.

(a) *Metal cells*

The construction of the metal cells is described in detail in an earlier report[3] so that only the main points need now be summarized.

Copper or V_2A-steel (stainless steel) cylinders have 2 or 4 channels (diameter 5 mm)bored through their lengths. A platinum wire is tautly centred—by means of beryllium–copper springs—through each channel. The channels are sealed by means of screw-caps, silver-soldered to the cylinders.

The construction of a copper, two-channelled cell is depicted in *Figure 2* (see also *F* in *Figure 1*).

The current lead-in wires are passed through oblique bores in the cylinder. The insulation consists of tubes sealed with the packing material Araldite.

The metal thermal conductivity cells, especially those of copper, can be employed for long, unbroken periods, at temperatures of 250°C.

More efficient detection is obtained with glass thermal conductivity cells (*Figure 3*). As might be expected these are much more easily and quickly constructed. They are, furthermore, capable of withstanding higher temperatures of up to 300°C. Working temperatures are more restricted with the metal cells as, at temperatures above 250°C, their Araldite packing begins to melt and leak.

The platinum lead-in wires have a diameter of 0·6 mm with normal glass and 0·3 mm with Pyrex and are, in both cases, simply fused into the glass.

The lead-ins are attached to the detection wires by clipping together, the working temperatures being too high for soldering.

The copper cell No. 2 was compared with the glass cell No. 4 for *detection sensitivity*. It was found that for an extremely wide temperature range (20–250°C), both cells possessed approximately equal sensitivity (see *Table II*).

The results justify the conclusion that horizontal positioning of the channels is better than vertical positioning. This is in accordance with the findings of Phillips[4].

Table I. Katharometers

No.	*Thermal-conductivity cell*	*No. of channels*	*Channel diam.* mm	*Platinum wires*			*Remarks*
				Diam. mm	*Length* mm	*Resistance* ohms	
1	*Copper*	2	5	0·05	100	ca. 7	*Low sensitivity*
2	*Copper*	2	5	0·02	100	39	
3	*Stainless steel*	4	5	0·02	100	ca. 35	*For corrosive compounds*
4	*Glass*	2	5	0·02	100	33	*Zig-zag wires give slight improvement in sensitivity*
5	*Glass*	2	7	0·02	300	105	
6	*Glass*	2	2	0·02	100	32	*Low dead-volume allows better separations and higher sensitivity*
7	*Glass*	2	0·67	0·02	100	32	

Figure 2. Metal thermal conductivity cell

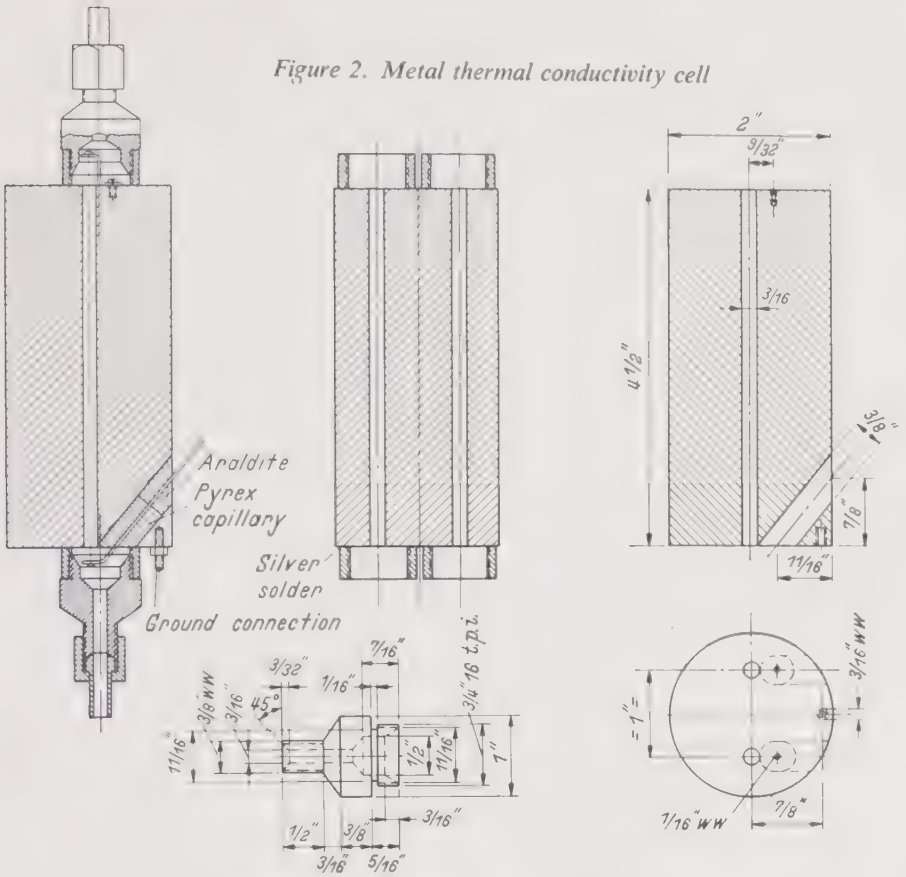

Figure 3. Glass thermal conductivity cell

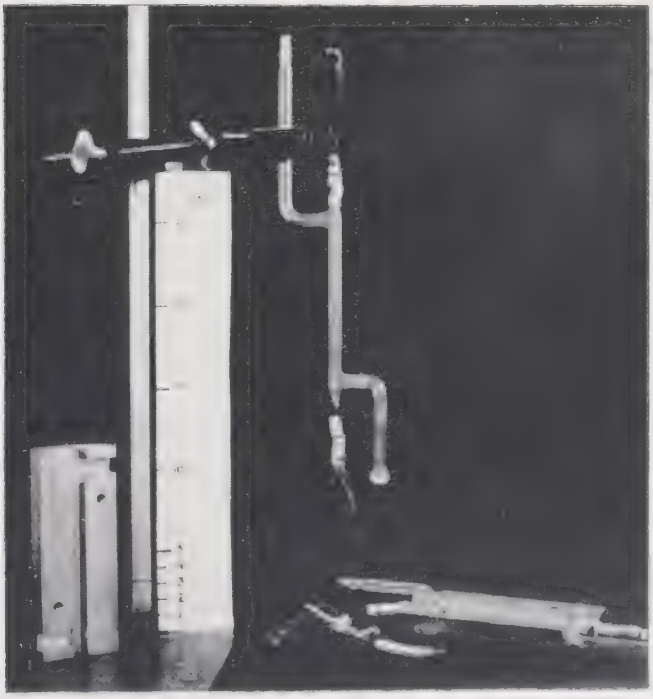

Table II. Comparison of Cells of Copper and Glass

Compound	*Bridge voltage*	*Temperature of cell* C	*Recorder-readings* *		
			Glass cell		*Copper cell*
			Hor.	*Vert.*	*Vert.*
7·5 μg *Methyl caproate*/ml *nitrogen*	8	20		16	16
	8	20	23	16	
	12	20	32	20	
	16	20	24	2	
ca. 60 μg *Methyl butyrate*/ml *nitrogen*		164		40	37

* 100 units = 2·5 mV

Inoperative space

A glass column is used in conjunction with the glass cells. The column is made up of sections joined together by means of ball ground-joints (*Figure 4*).

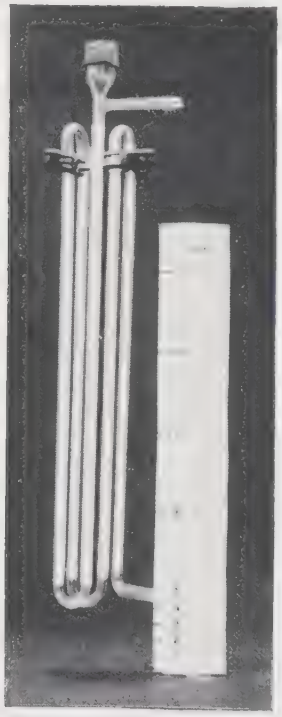

Figure 4. Glass column

The column has a diameter of 5 mm and a total length of 125 cm; it is heated with heating-tape. The column is attached to the detector channel by a spherical ground-joint. In this apparatus the dead-volume is 0·2 c.c., as compared with 3·5 c.c. in the metal version.

3. Stationary Phases for Use at High Temperatures

It is sometimes desirable to collect the substances emerging from the column in order that they may be further analysed by other methods (e.g. u.v. and i.r. spectra; mass spectrography). It is then of primary importance to ensure that these substances are not polluted by products originating from the column filling.

In this connection, our experience is that under conditions of high temperatures and fine distribution many inert and heat-resistant substances are prone to give off minute amounts of matter to the nitrogen stream.

From this aspect paraffin oil and paraffin wax (m.pt 60–80 C) are quite unsuitable as stationary phases at temperatures above 150–170°C. Even Silicone high-vacuum oil gives off low polymer products (identified by i.r. measurements).

In the search for inert materials which exhibit no signs of instability at high column-temperatures over prolonged periods, several substances were tested. These are shown below together with the amounts (where these were determined) which emerged from the column in 1 hour, at temperatures of 210–250°C and a gas flow rate of 15 ml/min:

1. Polythene (Mean mol.wt 30,000) (8 mg/h)
2. Polythene (Mean mol.wt 40,000)
3. Low pressure polythene (Ziegler)
4. Polytrifluoro-chloro-ethylene (Hostaflon)
5. Silicone elastomer D.C. No. 152
6. Silicone elastomer D.C. No. 123 (3 mg/h)
7. Silastomer D.C. No. 156 (8 mg/h)
8. Silastomer D.C. No. 132
9. Silicone grease (Wacker)
10. Silicone gum (Dow–Corning)
11. Apiezon M grease (5 mg/h)

Many experiments were conducted with various percentages of these substances as stationary phase on Celite 545. Some of the results are shown in *Figure 5*.

As will be seen from these results, most of these substances gave excellent separations of substances with low boiling points. For the separation within a reasonable time of the higher fatty acid esters (C_{16}–C_{18}), however, only a few of these substances were suitable, namely:

1. Polythene (mol.wt 30,000), 10 per cent on Celite (*Figure 5*, No. *4*).
2. A good silicone grease, 10 per cent on Celite (*Figure 5*, No. *6*).

Silicone greases show great variations in retention times between production batches, e.g. *Figure 5*, No. *5* shows a silicone grease of poor quality.

4. Sensitivity of the Thermal Conductivity Cells

As is generally known, the Martin and James gas-balance-cell[5] has unusually high detection sensitivity (±1–10 microgrammes).

This applies also to the Martin and Smart i.r. detection apparatus[6], with which, however, the loss of the separated substances is a serious disadvantage.

With the standard thermal conductivity cell, lower methyl esters can be analysed[1] in amounts of 10–30 microgrammes. A favourable signal-to-noise ratio, however, allows greater amplification (obtainable by increasing the

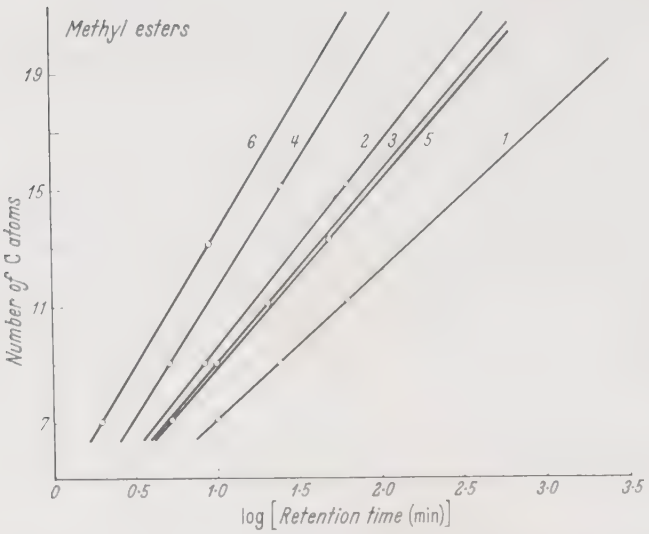

Figure 5. Stationary phases for use at high temperatures

Expt No.	*Immobile phase*	*%*	*Column temp. °C*	*Flow rate ml/min*
1	*Apiezon grease*	30	208	15
2	*Apiezon grease*	9	208	14·5
3	*Polythene 30,000*	23	205	14·5
4	*Polythene 30,000*	9	210	15
5	*Silicone grease*	9	214	12
6	*Silicone grease*	9	214	12

voltage in the detection wires) and this in turn facilitates analysis of even smaller amounts. This effect can be seen in *Figure 6*, in which the analysis of 400 microgrammes methyl caproate at 4, 8 and 12 V is represented. In this series of experiments the sensitivities relevant to these voltages were 3·4, 26·6 and 59·4 mV min, respectively.

As the temperature of the cell as a whole rises, however, the resistance of the detection wire increases, resulting—when the applied voltage is kept constant—in a reduction in the temperature of the latter relative to the channel wall, and a consequent reduction in sensitivity. (For this temperature effect see *Table III* and *Figure 6*, *a* and *b*.)

Table III. Effect of Change of Temperature

Voltage in platinum wire	*Increase in temperature of wire at cell temperatures of:*		
	23°C	100°C	190°C
2	68		
4	97	64	42
6	161	110	78
8	218	152	102
10	283		

It is obvious therefore that the detection sensitivity cannot be as great with substances with high as with those with low boiling points.

Using the 1 mV recorder, 16 V and a cell temperature of 130 C, as little as 4 microgrammes methyl caproate can be detected readily in the metal apparatus. When dealing with such minute amounts of substance the volume of the detection cell becomes an important factor as the zone emerges in a

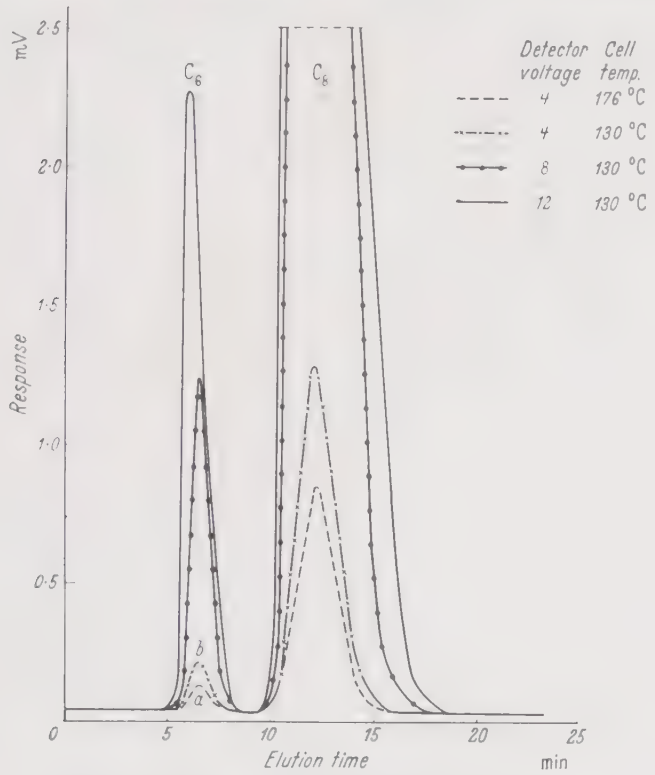

Figure 6. Effect of cell temperature on sensitivity

gas volume which is too small to fill the cell. This led to the construction of a glass katharometer with a diameter of 0·67 mm through which a wire of 20 μ diameter is stretched. With this katharometer and using a 1 mV recorder and a bridge voltage of 8 V a minimum amount of 0·5 microgramme methyl caproate could be detected.

5. Peak Inversion in the Thermal Conductivity Cell

It was observed that at high temperatures a number of substances (e.g. alcohols) gave negative peaks. This phenomenon was further investigated using methanol as the experimental substance. From *Figure 7* it can be seen that as the working temperature rises the begin- and end-phases of the peaks become increasingly more negative, until the positive peak—which appears at the maximum concentration—has completely disappeared. An obvious explanation is that these peak inversions are caused by the dehydrogenation of the compounds concerned at the surface of the hot platinum wire.

The emerging fractions were collected and tested for aldehyde content with Nessler's reagent.

It appeared that the progressively more pronounced peak inversions went hand-in-hand with the increasing aldehyde contents of the emerging fractions. As the chain lengths of the alcohols increase so the peak inversions become less pronounced, and higher wire temperatures are required to bring about the inversion. The possibility of a catalytic effect of the copper cell walls being responsible for this can be disregarded as the same phenomenon is observed when a glass katharometer is used.

That the *wire temperature* is indeed the determining factor and, conversely that the temperature of the surroundings (gas and walls) is of no importance

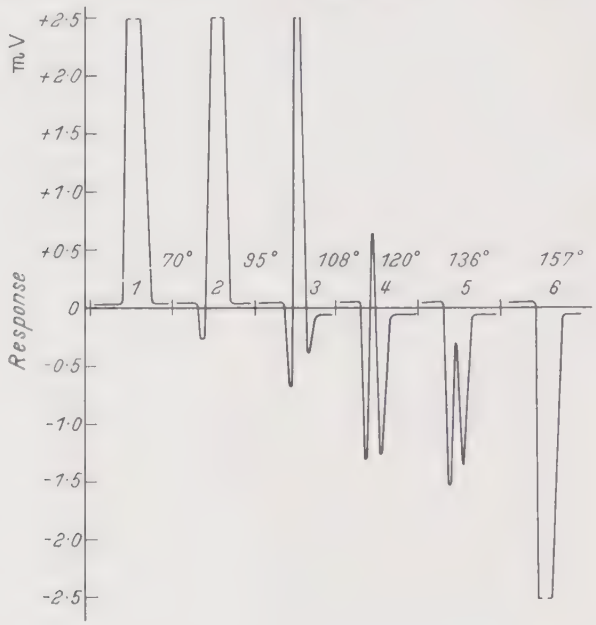

Figure 7. Effect of wire temperature on peak inversion

in this respect, could be demonstrated in yet another way. With a cell temperature of 136°C, a wire temperature of 193°C and a bridge voltage of 8 V, an identical peak form was observed as with a cell temperature of 158°C, a wire temperature of 195°C and a bridge voltage of 4 V.

This degradation occurring in the vicinity of the platinum wire was observed with a number of compounds, namely:

Methanol	(160°C)	*cyclo*Hexane	(245°C)
Ethanol	(186°C)	Ether	(215°C)
Butanol	(220°C)	Light petroleum	(245°C)
Glycol	(230°C)		

The temperatures at which the inversions first commenced are shown in parentheses.

Although *cyclo*hexane exhibited the peak inversion, no such inversion could be observed with benzene up to the maximum applied temperature of 275 C.

An alternative explanation for the peak-inversion phenomenon might be based upon the following reasoning.

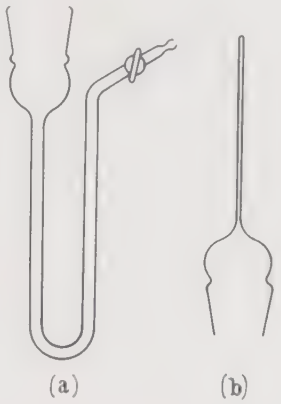

Figure 8. Fraction collectors

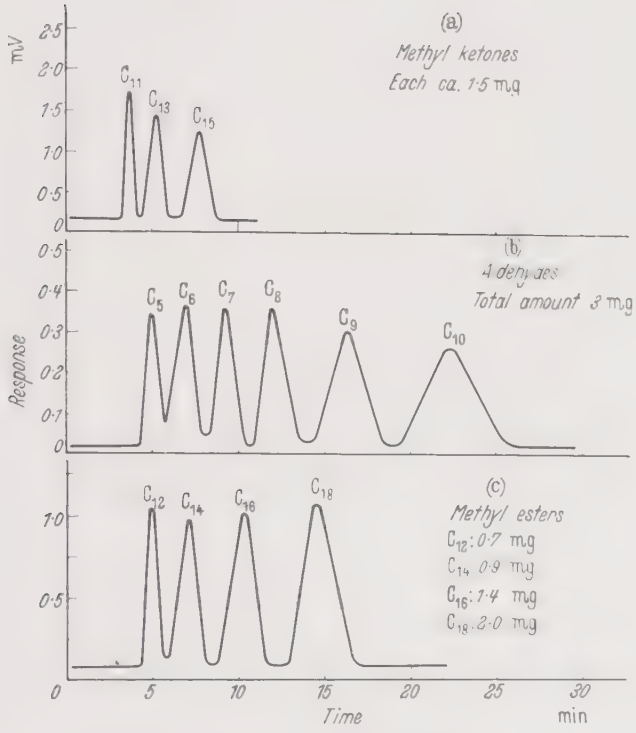

Figure 9. Typical analyses

Substance	*Immobile phase*	%	*Column temp.* °C	*Flow rate* ml/min	*Column diameter* mm	*Outlet pressure* mm Hg
Methyl ketones	*Silicone grease*	9	209	15	10	760
Aldehydes	*Silastomer DC 156*	33	180	13	10	760
Methyl esters	*Silicone grease*	9	228	6	5	110

As has been established by Ishikawa and Yagi[7] for a mixture of carbon monoxide and carbon dioxide, the thermal conductivity curve relevant to a mixture of two gases can show a maximum under certain conditions. It might therefore be argued that the peak inversions observed in this investigation are attributable to very pronounced maxima in the gas mixture curves, due to the influence of high temperatures. However, as stated above, it has been established that these peak inversions are solely dependent upon the detector-wire temperature and in no way upon that of the gas mixture. This signifies that in thermal-conductivity measurements the temperature of the wire will, in general, be the decisive temperature factor for the determination of the thermal conductivity coefficient.

Despite the fact that degradation was unquestionably demonstrated in these experiments the possibility that this hypothesis offers an explanation for the peak inversions in other cases should not be disregarded.

6. Apparatus for the Collection of Fractions

When it is desirable to collect various emerging fractions separately in order that they may be further investigated, advantageous use can be made of the apparatus depicted in *Figure 8* which is particularly suited to the extremely small amounts usually involved.

The emerging fraction is collected at −80°C [*Figure 8*(a)] which causes it to be spread over a relatively large area.

By the application of 'freeze-drying' the fraction is then collected in a suitably placed capillary tube [*Figure 8*(b)].

7. Analysis Results

A number of analyses carried out in the course of these investigations are shown in *Figure 9*.

The authors wish to express their thanks to Mr Keyer and to Mr Wenckebach for their aid in the construction of the katharometers and also to the management of Unilever N.V., Rotterdam, for their kind permission to publish this text.

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DISCUSSION

A. T. James: I would like to emphasize at this point that in the analysis of the long-chain fatty acids, whilst for industrial purposes it is adequate to carry out analyses in fifteen minutes, the large number of components present in natural fats cannot be resolved in such short times. The naturally occurring fatty acids are not, as is stated in all text books, only the even-numbered acids. The gas–liquid chromatogram has demonstrated the presence of odd-numbered straight-chain saturated acids, odd- and even-numbered branched-chain saturated acids and also odd-number

unsaturated acids. An example of this is shown in *Figure 10* which shows the acids present in the skin secretion of the rabbit (from Wheatley, V. R. and James, A. T. *Biochem. J.* In press).

The position of an unsaturated acid on the chromatogram will define the number of carbon atoms in the molecule but cannot give precise information on the position of the double bonds. This can be accomplished in the following manner. The peak emerging from the chromatogram is condensed by passing the gas stream through a tube packed with defatted cotton wool wetted with methanol or ethanol. In this way

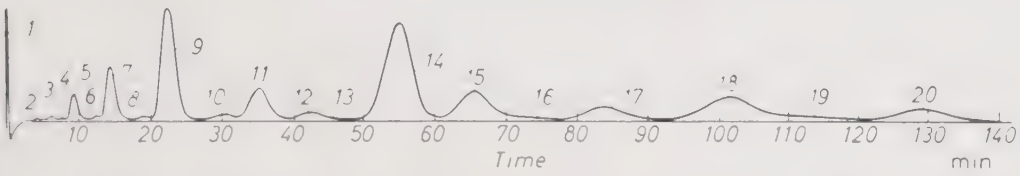

Figure 10. Fatty acids from rabbit sebum. Temperature 197°C. *Stationary phase: aromatic extract of lubricating oil. Pressure* 75·5 cm Hg. *Flow rate* 98 c.c./min. *Load* 4·8 mg

1, Air; 2, n-C_{10}; 3, n-C_{12}; 4, iso-C_{14}; 5, n-C_{14}; 6, iso- or ante-iso-C_{13}; 7, n-C_{13}; 8, iso- or ante-iso-C_{14}; 9, n-C_{14}; 10, iso- or ante-iso-C_{15}; 11, n-C_{15}; 12, Highly branched C_{16}; 13, iso- or ante-iso-C_{16}; 14, n-C_{16}; 15, Highly branched C_{17}; 16, iso- or ante-iso-C_{17}; 17, n-C_{17}; 18, Highly branched C_{18}; 19, Mono-unsaturated C_{18}; 20, n-C_{18}

the mists normally encountered in cooling gas streams containing high molecular weight substances can be removed. The material is washed from the condenser with ether or any suitable solvent, the solvent evaporated and the remaining acid is then oxidized by permanganate or by ozonolysis followed by fission to produce mono- and di-carboxylic acids. These are re-esterified to the methyl esters and identified by running on the gas chromatogram. In *Figure 11* is shown how the mono- and di-carboxylic acids can be resolved on a 4 ft Apiezon M column at 197 C.

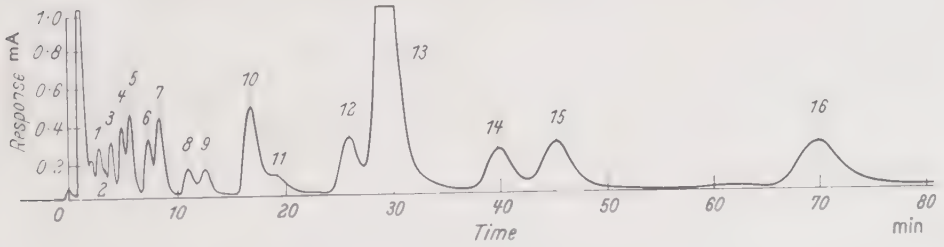

Figure 11. The separation of mono- and di-carboxylic acids as methyl esters. Stationary phase: Apiezon M vacuum stopcock grease (2–10 g *Celite* 545)*; column length* 4 ft*; temperature* 197°C*; nitrogen pressure* 23 cm Hg*; exit pressure, atmospheric. Load* 0·34 mg *mixture. Detector, gas density meter*

1, n-*Hexanoic; 2, Succinic; 3,* n-*Heptanoic; 4, Glutaric; 5,* n-*Octanoic; 6, Adipic; 7,* n-*Nonanoic; 8, Pimelic; 9, Decanoic; 10, Suberic; 11,* n-*Undecanoic; 12, Azelaic; 13,* n-*Dodecanoic; 14,* n-*Sebacic; 15,* n-*Tridecanoic; 16,* n-*Tetradecanoic*

C. H. Bosanquet: Concerning the relative merits of helium and nitrogen as carriers, I consider it very dangerous to assume a conductivity equal to the weighed mean of those of the components of the mixture.

Table III on page 78 and the curves on page 79 in Harvey and Morgan's paper show that for small quantities of methanol in nitrogen the procedure will be not merely inaccurate but between 100 and 250 C it will predict an effect of the wrong sign.

G. Dijkstra: It certainly is not correct to use the data for thermal conductivities

at room temperature for an accurate assessment of the relative value of nitrogen and helium for detection purposes. These data show, however, that the fairly widely held belief that helium or hydrogen increase detection sensitivity in katharometers by a factor of 6 or 7 over that obtained with nitrogen as a carrier gas is fundamentally wrong.

W. A. WISEMAN: With helium and nitrogen much depends on the compounds which you are trying to detect; e.g. with methyl alcohol it is almost impossible to obtain a response at 110 C, but using helium it gives a very satisfactory response indeed. Using ethyl alcohol at 110 C, for instance, helium does give a sixfold increase in sensitivity; at 90 C this is very much less than a sixfold increase. With ethyl acetate at 110 C it is about 1·3 times the sensitivity using helium as it is using nitrogen.

A. I. M. KEULEMANS: (*1*) The six straight lines drawn in *Figure 5* (page 228) refer to three different column liquids. I would expect the lines *1* and *2* referring to Apiezon grease and lines *3* and *4* referring to polythene 30,000 to be parallel. Can any explanation be offered for the differences of their slopes?

(*2*) When discussing Dr Herington's paper, Dr Dunn used the formula for the partition coefficient

$$k = M_{\text{solvent}}\, RT/\gamma^0 p^0$$

where M_{solvent} is the number of moles of solvent per unit volume. The formula explains the fact that for a homologous series of solvents the partition coefficient (or retention volume) increases with decreasing molecular weight of the solvent. Apparently the number of moles per unit volume of polythene 30,000 is very small. Nevertheless the retention volumes are appreciable. I think that the high solubility of the fatty acids in polythene is worth noting.

G. DIJKSTRA: I think that in *Figure 5* we have a comparison between two percentages of Apiezon grease and polythene and this shows that if you have more of the immobile phase it will take you a longer time to elute the substances. I thought it was expected that if you decrease the amount of immobile phase you will get a quicker elution. You may lose some separating power. That holds in the same way for the second phase you mentioned. Is that right?

A. I. M. KEULEMANS: I did not expect that the slope of these lines would be different for the same liquids. The amount of stationary liquid used is different so I would expect that the slope would be equal from what I have seen of all these plots and from what we have heard here. So I ask whether you have an explanation for the difference in slope.

G. DIJKSTRA: We only looked into the fact that it became much quicker and we have not paid any attention to the slope of the lines.

20

THE CONCEPT OF THE CHROMATOGRAPHIC SPECTRUM OF GASES AND VOLATILE MATERIALS

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The chromatographic spectrum of gases and vapours is a graphic system of characteristic sorption data which permits a prediction of the separation of individual compounds and calculation of the optimal chromatograph columns, as well as a comparison of abilities of the different chromatographic techniques.

The position of an individual compound in the chromatographic spectrum is given numerically by the number of millilitres of carrier gas necessary to carry one molecule of the given compound through an ideal column containing 1 ml or 1 g of a stationary phase (such as an adsorbent, or liquid-wet filling). This volume, denoted *U* by the author, is constant for a given system.

The relation of the structure of some gases and vapours to their position in the chromatographic spectrum is discussed. On this basis various techniques of gas–liquid partition chromatography, as well as various techniques of adsorption chromatography, are compared and their range of usefulness shown.

DURING recent years, a series of methods of chromatographic separation and analysis of gases and volatile materials has found large development. They are the adsorption and partition methods. The first procedure utilizes the sorption effect on active surfaces of some substances and it includes some variants: frontal chromatography[1], displacement chromatography[1-4] and elution chromatography[4–12] (a selection of the main literature only). The other way uses the dissolving abilities of the liquid[13] or the film of a less volatile liquid on an inert carrier[14–16].

Development of the methods under consideration offers a large amount of experimental material. The great variability of experimental conditions gives us broad possibilities in analytical practice but, on the other hand, it renders comparison of the results, reached by various authors, more difficult. For a rational selection of convenient techniques and working parameters, it is necessary to find a suitable basis for comparison. At present, an effort is seen[14,17,18] to find the uniting principles for a systematic ordering of the results reached. These studies refer exclusively to gas–liquid partition chromatography.

A chromatographic spectrum of gases and volatile materials will be discussed which enables a graphical survey of the quantitative arrangement of gases and vapours to be made. From their positions in the spectrum, it is

possible to obtain information on the separating possibilities of individual compounds, on the calculation of optimal chromatograph column sizes and on the mutual combination and mixing of the fillings. The molecular character of the compounds is reflected in the position of the individual compounds within the spectrum. It is thus possible to compare the convenience of individual methods to the special solution of preparative or analytical problems.

The present paper comprises new material from the field of elution chromatography on adsorbents, as well as our experiments from the field of gas–liquid partition chromatography.

Characteristic Chromatographic Data

The position of the individual gas or vapour in the chromatographic spectrum is given numerically by the number of millilitres of carrier gas, reduced to normal conditions, which are necessary for the carrying of the given compound through the ideal column which contains 1 ml or 1 g of a stationary phase (an adsorbent or a liquid-wetted carrier). This value, denoted here by U_{ml} or U_g, respectively, and called the adsorptivity of the adsorbent, is corrected for the pressure conditions on the column, as James and Martin[14], and Littlewood, Phillips and Price[19] show. It corresponds with the term of the fully corrected retention volume, V_g, introduced into the practice of gas–liquid partition chromatography.

The relation of the U value to the adsorption energy, expressed as the difference of the adsorption heats, is formulated

$$\Delta\lambda = RT \ln U_2/U_1 \qquad \ldots.(1)$$

where $\Delta\lambda$ is the difference between the adsorption heats of the gases 1 and 2, R is the universal gas constant, and T is the absolute temperature. There is a similarity with the Martin equation

$$\Delta A = nRT \ln c_1/c_2 \doteq RT \ln V_{g_2}/V_{g_1} \qquad \ldots.(2)$$

where ΔA is the work necessary for reducing 1 mole of substance from one phase into another, in partition chromatography.

Formerly[6], we could show that the U value is well reproducible at various rates of the carrier gas (0·3–1·5 ml/s). Littlewood, Phillips and Price described[19] a good reproducibility of the V_g values with various column fillings. Now, let us show that the values V_g correspond well even when chromatographing under various rates of carrier gas (*Table I*) and various pressure conditions (*Table II*).

Now, it only remains to mention the degree of reproducibility of the V_g values at various amounts of the wetting liquid. James and Martin[14] recommended using inactive substances (e.g. Celite) as carriers. In this case, the coincident values for the corrected retention volume per gramme may be reached at a full utilization of the liquid film only. As soon as the carrier is oversaturated, the V_g values decrease and the separation becomes incomplete. At an insufficient surface filling, the V_g values remain unchanged.

However, we have used even the surface-active substances as carriers of

Table I. Influence of Rate of Carrier Gas on Reproducibility of V_g Values

Column 180 cm; diameter 0·6 cm; filling 8·18 g di-*n*-amyl phthalate on 38·7 g sodium zeolite of grain size 0·2–0·4 mm; temperature 40 C

Streaming velocity N ml/s	V_g^{20} N ml/g *Di-n-amyl phthalate at* 40°C				*Pressure in* torr			*Correcting value*
	C_2H_6	C_3H_8	*iso*-C_4H_{10}	*n*-C_4H_{10}	*on flowmeter*	*inlet of column*	*outlet of column*	
0·632	1·59	4·89	11·3	16·5	1040	951	771·5	0·8919
0·542	1·74	5·04	11·5	16·8	1038	924	768	0·9058
0·451	1·77	4·98	11·3	16·1	1040	904	771·5	0·9184
0·361	1·69	4·95	11·6	15·7	1040	877	771·5	0·9340
0·276	1·67	5·31	11·55	17·0	1047	859	778	0·9499
0·180	1·65	4·74	10·9	15·7	1040	829	771·5	0·9634
Average	1·77	4·99	11·35	16·3				

Table II. Influence of Pressure at Flowmeter in front of Column on Reproducibility of V_g Values

Technical conditions as in *Table I*

Streaming velocity N ml/s	V_g^{20} N ml/g *Di-n-amyl phthalate at* 40°C				*Pressure in* torr			*Correcting value*
	C_2H_6	C_3H_8	*iso*-C_4H_{10}	*n*-C_4H_{10}	*on flowmeter*	*inlet of column*	*outlet of column*	
0·488	1·74	4·84	10·8	15·7	945	923	777·5	0·9121
0·525	1·86	5·00	11·05	15·9	1007	932	777·5	0·9073
0·542	1·74	5·04	11·5	16·8	1038	934	768	0·9058
0·567	1·82	5·02	11·35	16·6	1089	939	777·5	0·9036
0·589	1·75	5·18	11·35	16·7	1131	944	777·5	0·9005
Average	1·68	5·01	11·21	16·3				

the liquid phase with success. The conditions on the wetting of such a carrier with the liquid are well characterized by the measurements in *Table III*.

It is evident that the liquid film is, to a certain extent only, reproducibly utilized. Above this limit the film is not homogeneous, the V_g values decrease, and the separation of the components is bad; below this limit, however, the film is not sufficient to cover the sorption-active surface and, therefore, the V_g values change; nevertheless, separation of the components remains sharp beyond this point and the adsorbent gets new properties.

Table III. Effect of Amount of Wetted Liquid on a Surface-active Carrier on Reproducibility of V_g Values

Column 180 cm; diameter 0·6 cm; filling dibutyl phthalate on sodium zeolite of grain size 0·2–0·4 mm; temperature 20°C

% *dibutyl phthalate film*	U_g^{20} *N* ml/g *dibutyl phthalate* 20°C			
	C_2H_6	C_3H_8	*iso*-C_4H_{10}	*n*-C_4H_{10}
32	1·64	5·15	10·5	—
30	1·75	5·40	12·2	19·5
27·5	—	6·35	15·0	22·6
25	2·14	6·99	16·2	24·2
22	2·10	6·90	16·4	24·8
20	2·10	7·01	17·5	25·4
17·5	2·39	7·66	20·3	—
15	3·10	9·57	25·0	34·0
12·5	3·40	10·7	27·6	—
10	3·71	13·7	34·6	45·0

Relation of Position of Individual Compounds in Chromatographic Spectrum to their Nature and to the Absolute Temperature

James and Martin[14] and other authors[17,19,20] found in gas–liquid partition chromatography that the logarithms of the V_g values are in linear relation to the number of carbons in a molecule. We also confirmed these observations in chromatography on adsorbents. A relationship was found for the gaseous paraffins and olefins and it was verified under various temperatures for polar and non-polar adsorbents (silica[9], zeolites[8] and activated charcoal).

In principle, it is possible to separate the individual members of the homologous series, regardless of whether the saturated or unsaturated hydrocarbons or the cyclic hydrocarbons or their derivatives (whether or not they be members of a group of substances chemically or physically related, as rare gases, halogens, etc.) are considered. It appears that gases of similar structure and molecular size have similar U values per gramme on non-polar adsorbents, even if they differ in their boiling points. On the contrary, gases with different structures differ greatly, even if their boiling points are the same (*Table IV*).

On polar adsorbents, the U values of various gases differ according to the energy of the C—C bond or the asymmetry of the molecule. Thus, their order in the chromatographic spectrum is less dependent on their boiling points or on their molecular sizes, but depends almost exclusively on their internal energy, given by the double or triple bond or by the electric asymmetry (*Table V*).

Supposing that the value of the adsorption heat is constant, it follows from equation (1) that the logarithm of the U value should be in linear relation to the reciprocal value of the absolute temperature. On experimenting with

Table IV. Correlation of U_g Values of Some Gases on a Non-polar Adsorbent

Activated charcoal Supersorbon HR, grain size 0·25–1·00 mm

Gas	U_g^{20} *N* ml/g *activated charcoal at* 20°C	*Boiling point* °C
Nitric oxide	6·20	−152
Carbon monoxide	6·71	−191·5
Nitric oxide	6·20	−152
Krypton	18·5	−151·2
Nitrous oxide	72·4	−89·5
Ethane	324·0	−88

Table V. Correlation of U_g Values of Some Gases on a Polar Adsorbent

Silica, grain size 0·25–1·00 mm

Gas	U_g^{20} *N* ml/g *silica at* 20°C	*Boiling point* °C
Ethane	10·0	−88·3
Ethylene	20·3	−103·9
Acetylene	55·8	−83·6
Propane	34·8	−42·1
cyclo*Propane*	57·5	−34·0
Propene	160·0	−47·7
Methylacetylene	>300·0	−27·5
Vinyl chloride	376·0	−14·0
Trifluorchlor-ethylene	90·6	−27·9

various adsorbents under different temperatures we confirmed[6,cf. 21] that this relation is very approximately linear. *Figure 1* represents the relationship of log U_g of some very different substances on silica to the absolute temperature.

It is known that August's empirical formula, as well as the relation obtained by integrating the Clausius–Clapeyron equation, states that the logarithm of the vapour pressure is reciprocally related to the absolute temperature. In coincidence herewith Hoare and Purnell[17] found a linear relation between the vapour pressure logarithm and the logarithm of the V_g values of some vapours. We found the same relationship in the chromatography on adsorbents for lower members of the homologous series of the hydrocarbons at the same temperature.

CHROMATOGRAPHIC SPECTRA OF GASES AND VOLATILE MATERIALS

The graphic system, showing the correlations described, may be represented with one or two vertical logarithmic axes. The positions of the individual

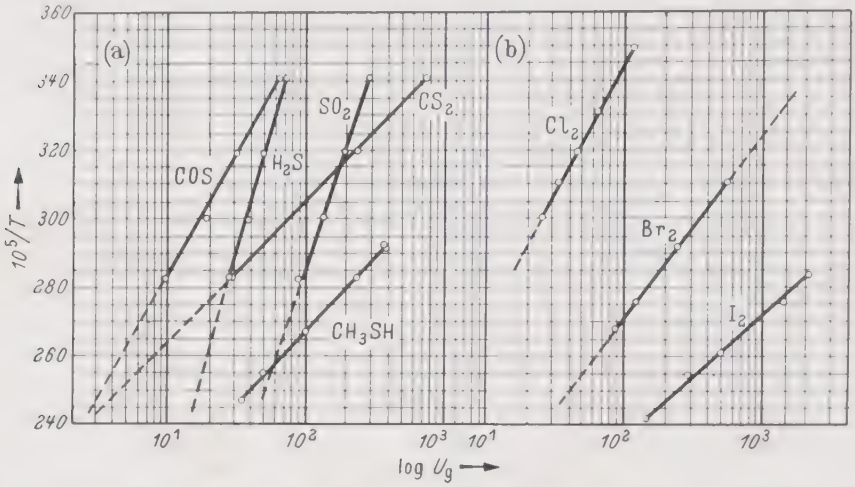

Figure 1. Inverse relation with polar absorbent of log U_g *of some* (a) *sulphur compounds* (b) *halogens, with absolute temperature* (*silica, grain size* 0·25–1·00 mm)

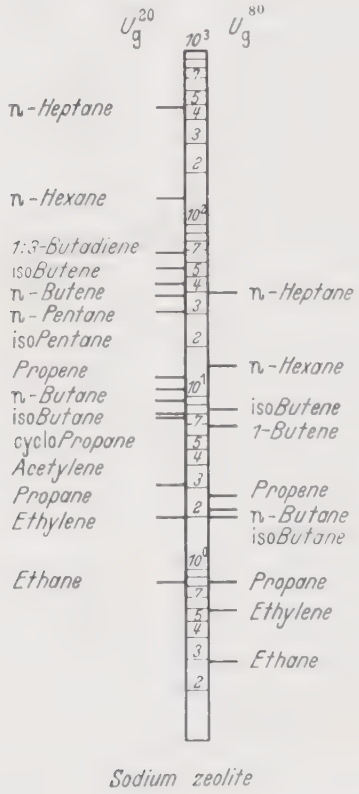

Figure 2. Chromatographic spectrum of gases

gases and vapours are represented with their value of U_g or V_g, respectively, at one or two temperatures, as shown in *Figure 2*.

According to the distance of the U_g logarithm, or V_g logarithm between

two adjoining homologous hydrocarbons with structural correspondence, it is easy to interpolate, as well as extrapolate, the characteristic elution values for the other members of a series. Similarly, according to the distance of the U_g or V_g logarithm at the temperatures, e.g. 20 and 80°C, it is possible to estimate the elution values within, as well as outside, this range. Likewise, the correlation of the U_g or V_g values with the corresponding vapour pressure of a substance at a definite temperature is easy.

The practical importance of chromatographic spectra for the correlation of various techniques is evident from *Figure 3*.

In this figure, the characteristic values of some gases and volatile materials on three adsorbents (activated charcoal, silica and sodium zeolite) and three spectra, estimated by means of partition chromatography on dibutyl phthalate, dinonyl phthalate and dimethylaniline, are compared.

Thus, adsorption chromatography on the activated charcoal seems the most convenient for the separation of permanent gases and for the concentration of small amounts of substances with higher boiling points. Partition chromatography on wetted carriers is most convenient for the separation of gases and volatile materials with higher boiling points. The chromatography on adsorbents of the sodium zeolite type is as promising for the separation as for the concentration of gases with higher boiling points and of highly volatile materials; it may contribute new possibilities even in combination with gas–liquid partition chromatography.

Now, let us turn to a detailed study of the spectra on sodium zeolite and dibutyl phthalate. On the dibutyl phthalate column perfect separation of the individual members of the paraffinic series, especially of *iso*- and *n*-butane, is possible. However, separation of ethylene from ethane, propene from propane and *n*- and *iso*-butene from *n*-butane is not feasible. On sodium zeolite the separation of individual members of the homologous series is also possible, but the separation of *iso*- and *n*-butane is more difficult compared with separation on the dibutyl phthalate column. On the contrary, separation of ethylene, *n*- and *iso*-butene from the paraffins is easy, but propene overlaps behind the *n*-butane.

Keulemans and co-workers[22] carried out the separation of paraffins and olefins on carriers wetted with liquids of a polar character; likewise, in our study[9], we found the advantages of polar adsorbents for the separation of saturated hydrocarbons from unsaturated ones, and of polar substances from non-polar ones. The effect of polar adsorbents with sodium zeolite is disproportionately stronger than may be attained with liquids of high polarities and of sufficiently high boiling points. It is possible to use with advantage a mixture of both types of chromatographic filling whereby the advantages of both techniques may be utilized. *Figure 4* illustrates these points.

The first chromatogram illustrates separations on the adsorption sodium zeolite column, the second the separation of the same mixture on the partition dibutyl phthalate column and the third chromatogram on the mixture of a free with a wetted adsorbent. It may be seen that at a perfect separation of the *iso*- and *n*-butane, caused by the dibutyl phthalate component of the mixture, the propene from the propane fraction is separated by means of the zeolite component, without colliding with the *iso*butane fraction. Likewise, both butenes present are extracted from the *n*-butane fraction.

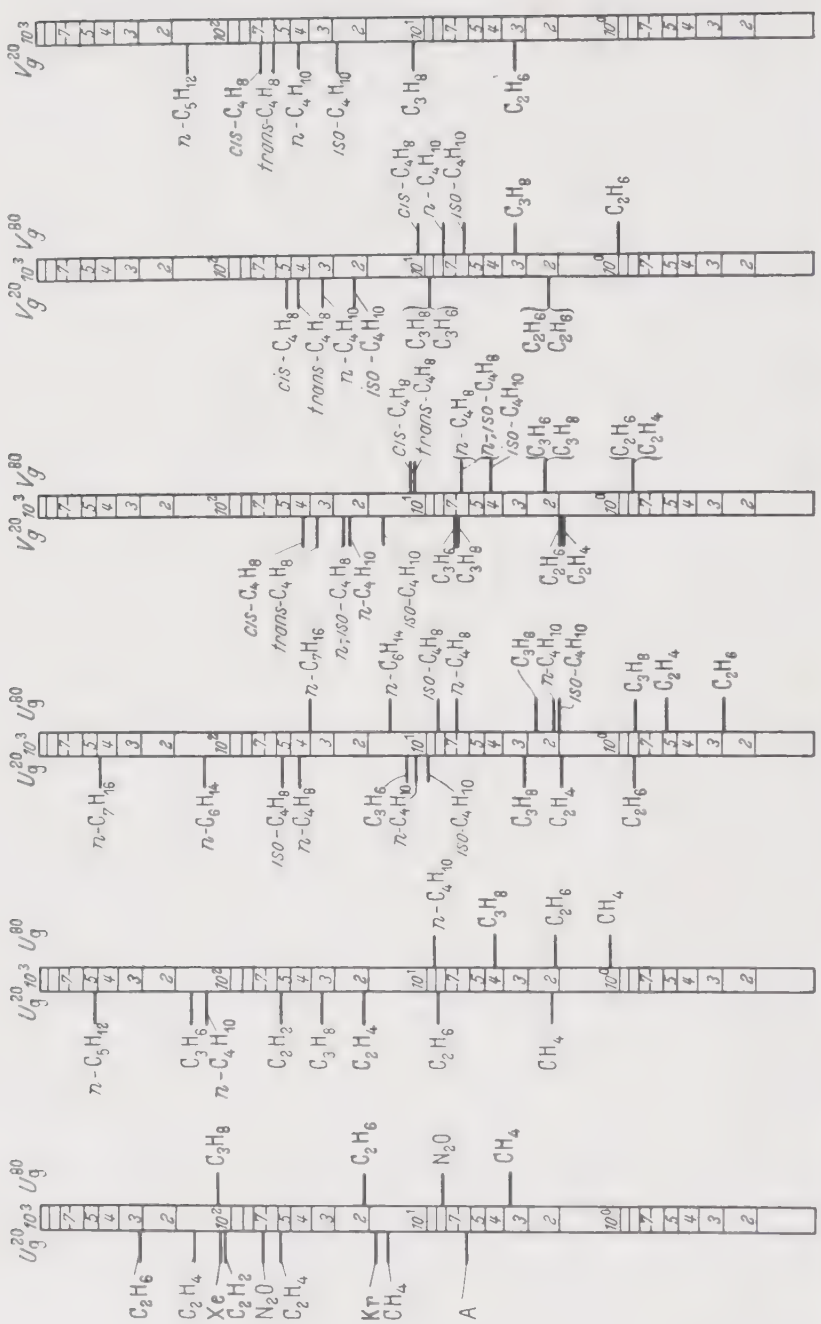

Figure 3. Correlation of various techniques according to chromatographic spectra

The calculation of a convenient combined filling, as well as of the time order of the components in the resulting chromatogram may be carried out from the positions of the components in the chromatographic gas spectrum.

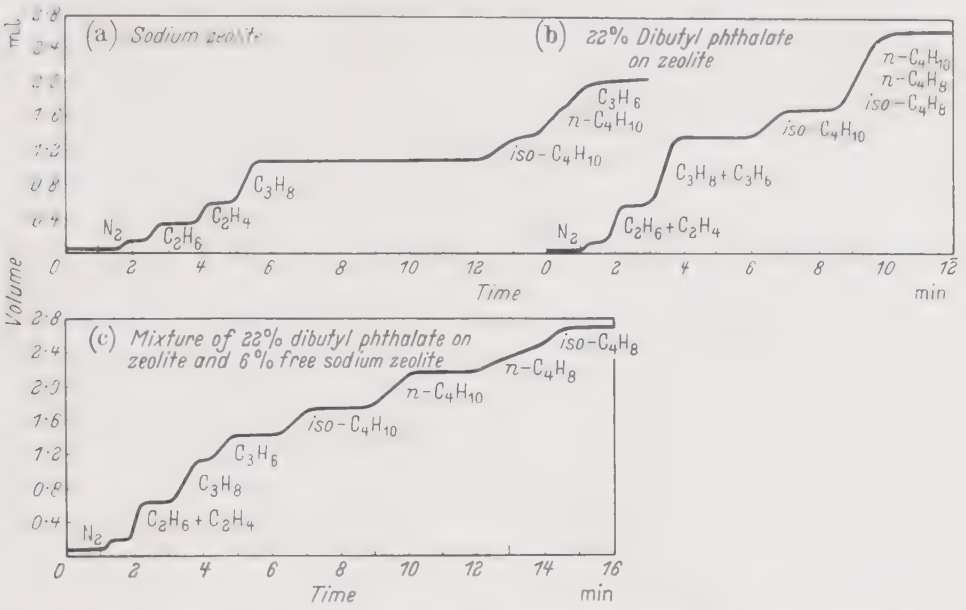

Figure 4. Chromatograms of a hydrocarbon mixture on various chromatograph columns (a) *Column* 180 cm; *diameter* 0·6 cm; *filling* 32·4 g *sodium zeolite with grain size* 0·2–0·4 mm; *atmospheric pressure* 763 torr; *pressure at column inlet* 157 torr, *at outlet* 40 torr; *temperature* 20 °C; *rate of flow of carbon dioxide* 0·546 *N* ml/s. (b) *Same column as* (a); *filling* 9·7 g *dibutyl phthalate forming a* 22 per cent *film on the sodium zeolite of grain size* 0·2–0·4 mm; *atmospheric pressure* 744 torr, *pressure at column inlet* 189 torr, *at outlet* 40 torr; *temperature* 20 °C; *rate of flow of carbon dioxide* 0·546 *N* ml/s. (c) *Same column as* (a); *a mixture of* 4·09 g *free sodium zeolite and* 8·09 g *dibutyl phthalate forming a* 22 per cent *film as* (b); *atmospheric pressure* 741 torr; *pressure at column inlet* 168 torr, *at outlet* 40 torr; *temperature* 20°C; *rate of flow of carbon dioxide* 0·544 *N* ml/s.

The data in *Table VI* show good agreement between the U_g, or V_n values calculated and found.

Table VI. Correlation of U_g Values calculated and found with mixed filling in the column.

Gas	U_g^{20} *sodium zeolite*	U_g^{20} *22% dibutyl phthalate*	U_g^{20} *For dibutyl phthalate mixed with 6% sodium zeolite*	
			Calculated	*Found*
Ethane	0·84	2·10	1·63	1·96
Ethylene	1·99	2·00	2·00	
Propane	3·10	6·75	5·92	5·95
Propene	12·4	7·00	8·22	8·75
iso*Butane*	9·7	16·4	14·0	14·8
n-*Butane*	11·1	24·8	21·7	22·5
1-*Butene*	45·7	27·0	31·2	31·5
iso*Butene*	64·5	27·0	35·5	34·8

The discussed configuration of gases and volatile materials according to their characteristic chromatographic constants, denoted as the chromatographic spectrum of gases and volatile materials (because of their independence of experimental conditions), thus determines the quantitative order of the individual components in the gas chromatography of both fundamental techniques: the adsorptive and the partitive one. It may, therefore, contribute to a systematic working up and ordering of the experimental material found in laboratories of all kinds.

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DISCUSSION

J. R. Young: Before commencing my remarks I would like to make two apologies. One, I was not among the lucky members who received copies of the papers so I must confess to not having read the papers in their pre-printed form. The other is that I am a vapour-phase chromatographist, if that is the correct term, of some three months standing, so if anything I say is common knowledge I hope it will be passed over.

The first point I would like to make is in the nature of a general query, and it concerns the possibility of separating the commoner permanent gases such as carbon monoxide, hydrogen, oxygen, etc., from the less volatile gases such as the C_2 compounds. Such work as we have been able to do seems to confirm the finding of Dr Janák who has found silica to be more suitable for the hydrocarbons and charcoal to be suitable for the permanent gases. But although there have been some publications by Patton on the separation of all the gases I mentioned on charcoal at an elevated temperature, unfortunately for the particular application I visualize this high-temperature working is prohibited because of destruction of some reactive

gas in the mixture. Moreover the use of any liquid column is also eliminated since reactive components would in all probability combine with the liquid on the support. So for this reason an absorption column working at a low temperature seems to be required, and if any members here have personal experience of this problem I would like some information.

The other point relates to an observation which we made during our early exploratory work which was made with a galvanometer detector, not an elaborate recording set-up, and deals with the relation between peak deflection and sample weight with hydrogen and nitrogen as carrier gases. If you plot the sample weight in milligrammes and the peak deflection in centimetres you get various straight lines for different substances for both hydrogen and nitrogen as carrier gases. If, on the other hand, one plots millimoles, or some suitable molar quantity, against peak deflection one gets for nitrogen a series of lines of differing slope. But for hydrogen, with some few compounds which we used—they were not compounds in which we are interested, they were actually pentane, diethyl, ether, acetone and chloroform (these were chosen as representing a variety of chemical types)—the millimoles plotted against peak deflection all fell close to the same line. I am not saying it was a good line, but there is no doubt that the same line did fit this group of compounds. One can relate this observation to a very naive theory of the operation of the katharometer detector which was being used. The essential part of this naive theory is based on the assumption that the thermal conductivity of a mixture of these gases with hydrogen is a simple weighted mean of the molar amounts. The relation breaks down in this case because of the much larger differential between the thermal conductivity of nitrogen and that of the substance used. In fact the relationship can only be approximate because it does depend on the relative constancy of differential thermal conductivity. However, I would like to know if anybody else has observed a linear relation of this kind, because it would have some bearing possibly on the method of reporting information. In this case the millimolar basis of comparison would be the same for a series of compounds of similar thermal conductivity.

A. I. M. KEULEMANS: (Acting as interpreter). The situation reminds me of a few years ago when I went into a cinema and saw a French film where the boy was expressing his feelings for a lovely girl in 500 to 600 words, and the sub-title said, 'I rather took a fancy to you'! I think what has just been said had better be considered as a contribution rather than a matter for discussion. It is best to say to Dr Janák that he agrees with his findings. (Dr Keulemans continued in German.)

F. VAN DER CRAATS: May I add some additional remarks with reference to Dr Janák's paper and his remarks on zeolites. I have not had sufficient time to study it all, but he separates hydrocarbons on zeolites and prefers activated carbon for the lighter permanent gases. We have found that synthetic zeolites, such as the Linde molecular sieves, with 4 or 5 Å mean bore diameter, are very suitable for this kind of separation. But I have to make the point here that using solid absorbents has a great influence on the kind of carrier gas you are using. Dr Janák always uses carbon dioxide in his experiments with zeolites. We found that molecular sieves, with carbon dioxide as a carrier gas, are completely saturated with carbon dioxide, and no further absorption of nitrogen, methane, and so on, occurred. So you can only use this absorbent with hydrogen or nitrogen as the mobile phase. Then, for instance, with molecules of 5 Å, you can make very nice separations of hydrogen, oxygen, nitrogen, carbon monoxide, and methane at normal temperatures. You cannot separate them on activated carbon or silica gel, but you can separate them quite easily with this type of molecular sieve. Compounds like ethane and ethylene at normal temperature are very strongly absorbed on zeolites, but by using carbon dioxide as a carrier gas in this case you can separate the C_2 and C_3 hydrocarbons. So here you have another point that by varying the nature of the carrier gas you can modify your absorbents. The zeolites

of course are also very important for separation of *iso* compounds from normal compounds, and even at high temperatures propane and normal butane are very strongly absorbed whereas *iso* compounds just come through like air. So you can make very quick determinations of *iso* compounds in quite a wide boiling range of *iso*-normal mixtures.

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VAPOUR PHASE CHROMATOGRAPHY ON ZEOLITES

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A description of adsorption chromatography of gases and volatile materials, using active aluminium silicates as adsorbents, is given. Carbon dioxide is used as the carrier gas, but other gases may also be employed (nitrogen, hydrogen, ammonia, etc.). The new possibilities of the active aluminium silicates are as follows.

(*1*) The polarity of the adsorbent requires that the order of the hydrocarbons, for instance, in the chromatographic spectrum of gases and vapours shall be similar to the order of the same hydrocarbons on silica gel; the adsorption heats of the individual hydrocarbons, however, have lower values than those on silica gel. The zones are narrow, the separation is sharp, and the time necessary for the analysis is short.

(*2*) The easy exchangeability of the sodium ion with other cations makes possible the introduction of ions of different radius. Thus the lattice may be so deformed that the pores resulting from the dehydration of the zeolite would have the defined sizes. These sizes may be so selected as to permit entry of straight-chain hydrocarbons into the pores and to check simultaneously the entry of branched-chain hydrocarbons.

(*3*) By introducing some ions affecting the chemisorption, the adsorption activity may be raised for gases and vapours of definite chemical nature.

We have found[1] that, in sorption on polar adsorbents like silica, the energy of the C—C bond or the polarizing ability of the molecule, respectively, is particularly useful in conjunction with the double or triple bond or with the asymmetry of the molecule. With increasing degree of unsaturation of the molecule (ethane–ethylene–acetylene or propane-*cyclo*propane–propene methylacetylene) or with increased electric asymmetry (trifluorchlorethylene–vinyl chloride) the adsorbability of the polar adsorbent grows.

To realize the optimal performance of chromatography, it is necessary to use adsorbents on which the separated volatile materials lie within that region of the chromatographic spectrum which is defined by U' values of the order $1–10^2$.

The term U is defined as the corrected carrier gas volume which is necessary for the elution of the chromatographed materials from 1 g (U_g) or 1 ml (U_{ml}) of the adsorbent to maximal concentration[2,3]. A correction is made for the dead-space of the measuring apparatus beyond the adsorbent column, as well as for the pressure difference between inlet and outlet of the chromatograph column and for the pressure difference from atmospheric pressure[4]. The U' value corresponds to the term V_g, used in gas–liquid partition chromatography and denoted as the fully corrected retention volume[5].

Thus, the easiness of separation of the individual compounds is not given by the absolute difference of their U values but by their ratio. Thus, for example on measuring, we found the differences of the U_g values for a pair of gases, methane–ethane on silica

$$U_{C_2H_6} - U_{CH_4} = 10{\cdot}0 - 2{\cdot}5 = 7{\cdot}5 \qquad \ldots.(1)$$

to be smaller than for the pair *n*-butane–*iso*butane

$$U_{n\text{-}C_4H_{10}} - U_{iso\text{-}C_4H_{10}} = 139 - 127 = 12 \qquad \ldots.(2)$$

Nevertheless, the former pair separates easily whereas the separation of the two isomeric butanes does not take place in practice.

Activated charcoal is therefore a suitable adsorbent for the separation of permanent gases[2] and silica for the separation of hydrocarbons. But, even on silica, the C_4 and higher hydrocarbons and other gases with boiling points near 0°C attain U values over 100. We searched for new adsorbents which would maintain the specific sorption quality (the polarity) at which, however, the absolute value of U_g would be lower. This condition is realized with the active types of alumina[6] and with some active types of silicates such as zeolites. The interest in both natural and synthetic zeolites as adsorbents of gases and vapours was increased principally by the studies of Barrer[7–9] (a selection of the literature only).

In spite of the fact that, theoretically, convenient properties may be expected with zeolites, these substances have not so far been utilized in gas chromatography. New possibilities are given (*a*) by the polarity of the adsorbents which raises relatively the U values for the unsaturated and polar substances at, in the main, absolute lower U values; (*b*) when the area of the surface and the size of the pores of the adsorbent give the possibility of separating the compounds in accordance with both the steric configuration and the molecular size; (*c*) when it is possible to insert new cations into the lattice by means of ion exchange whereby, for some compounds, considerable changes of U values may be reached.

Apparatus

The gas chromatograph consists of the following sections: source of the carrier gas, excess pressure adjustment, flowmeter, sample inlet, thermostatted column with adsorbent, and recording system.

A steel pressure vessel serves as source of the carrier gas. According to requirements, carbon dioxide, hydrogen, nitrogen, oxygen and the like are used. Carbon dioxide must be prepared with very high purity, either by means of decomposition of a carbonate or liquefaction of solid carbon dioxide in a pressure vessel (this procedure is described by Ray[11]).

Two types of recording system are in use: (*a*) the differential record and (*b*) the integral record. The differential recording system is based on the thermal conductivity of gases and vapours. It is built up with two electrically equalized cells in a simple bridge. We use a platinum wire, 0·05 mm in diameter and 220 mm in length, wound as a lamp filament. The response of the cell under these conditions is nearly immediate, as the cell dead-space is smaller than 0·8 ml. The integral recording system is based on measurement of volume of the component over the concentrated potassium hydroxide

solution wherein the carrier gas (carbon dioxide) is absorbed. The scheme may be seen in *Figure 1*. The increase of volume over the potassium hydroxide level in the azotometer (*A*), caused by the arrival of the gaseous fraction, disturbs the set pressure. The pressure change causes a movement of the equalizing liquid in the manometer (*B*) (mercury, diluted sulphuric acid) whereby the motor (*C*) is switched on and moves the piston (*D*). The movement of the piston which is in a defined relation to the increasing volume over the potassium hydroxide solution level is recorded mechanically at (*E*). The constant level of the potassium hydroxide solution is maintained with the compensating mercury piston (*F*), driven by the motor (*G*).

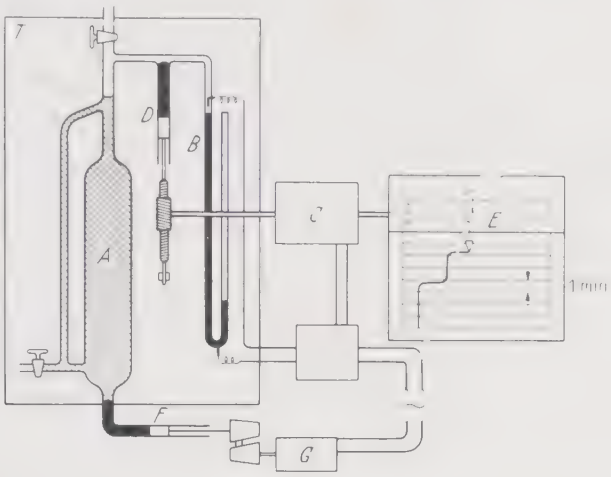

Figure 1. Indicating system for direct registration of gas volume

It is necessary to compensate (*a*) the increment of the gas volume, caused by small amounts of inert gases in pure carbon dioxide (generally less than 0·003 ml/min), (*b*) the increment of the potassium hydroxide solution volume, caused by the change of density of the solution during absorption of carbon dioxide (usually more than 0·01 ml/min).

Under these conditions, it is possible to work at temperatures (thermostat, *T*) up to 60 C and under reduced pressure down to 300 mm of mercury. On calculating, it is necessary, in extreme cases, to consider the correction for the water vapour pressure over the concentrated potassium hydroxide solution. The relative sensitivity of the measurement is not the same at the end as at the beginning. This way of indication is especially convenient for the separation and analysis of hydrocarbons and gases which are not soluble in potassium hydroxide.

Vapour Phase Chromatography on Sodium Zeolite

Sodium zeolite (commercial type 'Alusil') was used. It is a highly homogeneous porous white material (82 per cent free space at grain size 0·2–0·4 mm) of surface area 2×10^2 m^2/g. It is activated by heating for 3 hours at 270 C whereby it loses 14·5 per cent water. Activated zeolite has the following chemical composition: SiO_2 80·37, Al_2O_3 8·6, Fe_2O_3 0·15, Na_2O 6·69, K_2O 2·17, CaO 0·25, MgO 0·04, and SO_3 0·37 per cent.

The chromatographic spectrum of the hydrocarbons is illustrated in *Figure 2*. It is evident that sodium zeolite has very convenient properties for separating mixtures of saturated as well as unsaturated hydrocarbons. Because of its relatively low U_g values for hydrocarbons with five to seven C atoms in a molecule, it is as convenient for concentrating as for separating paraffins.

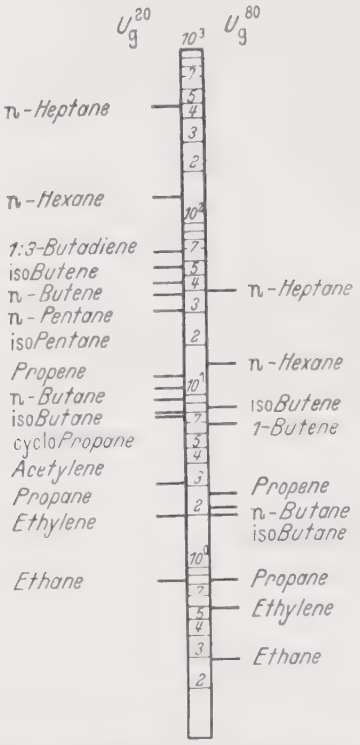

Figure 2. Chromatographic gas spectrum on sodium zeolite (carrier gas, carbon dioxide)

We studied, therefore, the behaviour of *n*-paraffins to C_7 in the temperature range 20–80°C.

In these values the internal structure of the hydrocarbon molecules is reflected. The formerly derived relation[2] between absolute temperature and U values

$$\log U = K \,.\, 1/T \qquad \ldots.(3)$$

was verified. *Figure 3* illustrates the linear relation of the U_g logarithm to $1/T$ in a sufficiently broad temperature range for all the hydrocarbons studied.

On following the increment of the U logarithm for the individual members of a homologous series, it will be seen that it fits the equation

$$U_n^t = U_a^t \,.\, q^{(n-a)} \qquad \ldots.(4)$$

where U_n^t is the U value per gramme of an adsorbent at temperature t °C for the nth member of a homologous series, U_a^t is the U value per gramme for the known ath member of a series under identical conditions, and q is a quotient, the value of which is given by

$$q = U_n/U_{n-1}$$

i.e.
$$\log q = \log U_n - \log U_{n-1} \qquad \ldots.(5)$$

The validity of this relation is demonstrated in *Figure 4*.

Estimation of higher hydrocarbons (gasoline) in natural gas

From *Figure 4*, the U_g values may be extrapolated to the temperature of −60 °C. They are for ethane 9, for propane 65 and for *n*-butane 450 *N* ml

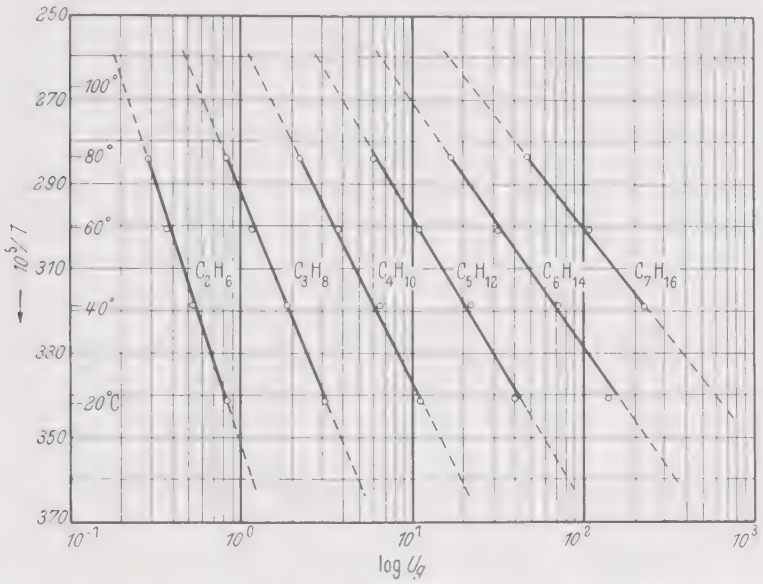

Figure 3. Relation between log U_g *of paraffins up to* C_7 *and absolute temperature (sodium zeolite; carrier gas, carbon dioxide)*

per gramme of zeolite. For the higher hydrocarbons the elution volumes are of the order 10^3 *N* ml/g. On this principle, it is possible to determine easily the higher hydrocarbons in natural gas under field conditions.

A U-pipe, filled with 2 g sodium zeolite of grain size 0·2–0·4 mm, is

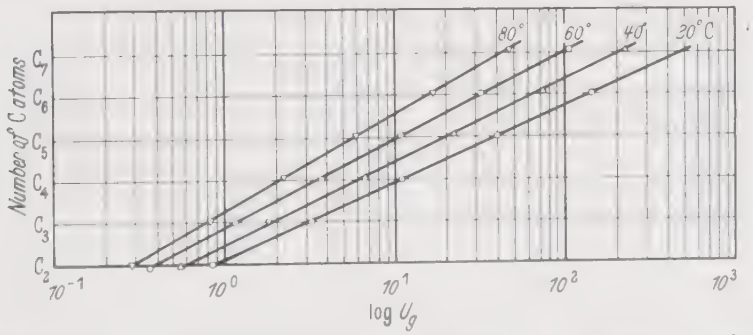

Figure 4. Relation between log U_g *and number of* C *atoms in molecule (sodium zeolite; carrier gas, carbon dioxide)*

cooled in a Dewar vessel in solid carbon dioxide. 10–100 ml natural gas is passed through the pipe the ends of which are closed (melted). In the laboratory, a column with a content of 4 g sodium zeolite is joined and the chromatographic separation is carried through at a temperature raised gradually to

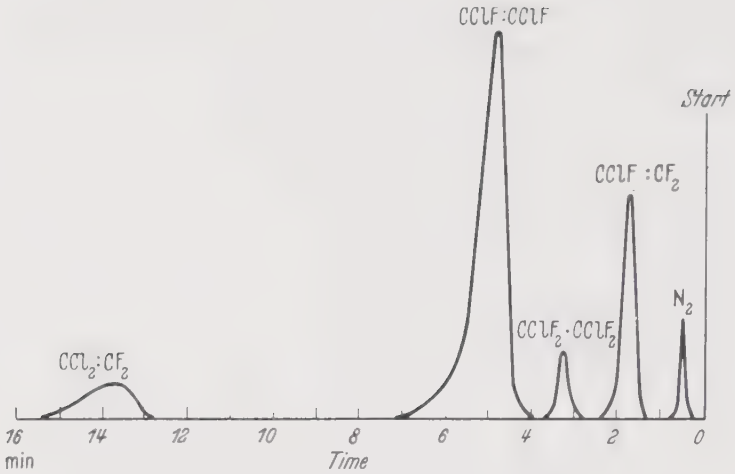

Figure 5. Separation of some Freons on sodium zeolite

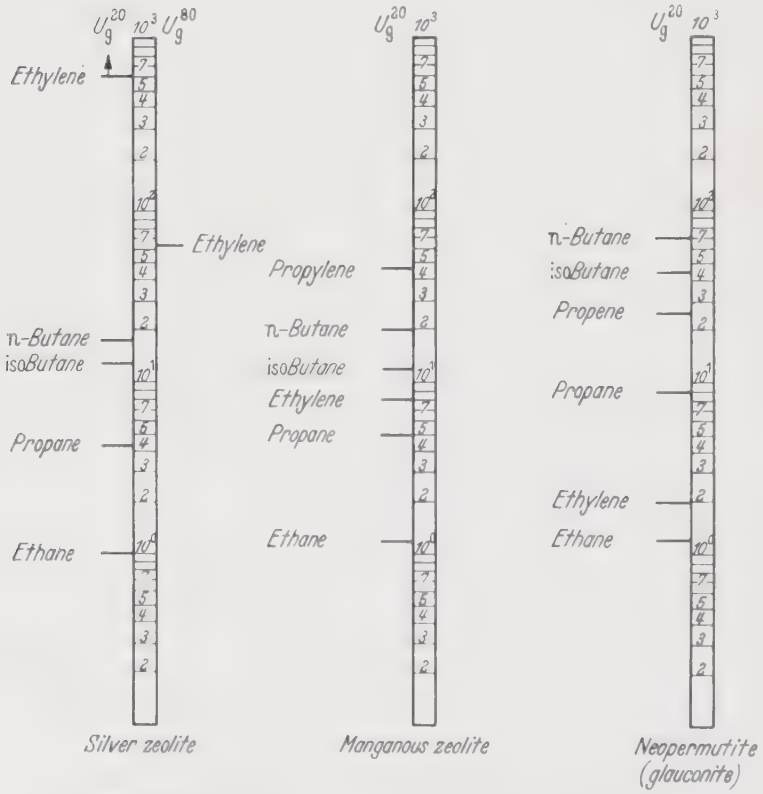

Figure 6. Chromatographic spectra of gases on substituted and natural zeolites (carrier gas, carbon dioxide)

80 C. The analysis lasts 20–30 minutes. The typical reproducibility is evident from *Table I.*

Table I. Reproducibility of the Determination of Higher Hydrocarbons in Natural Gas

Sample	C_5H_{12} g/*N* m³	C_6H_{14} g/*N* m³	C_7H_{16} g/*N* m³	C_8H_{18} g/*N* m³
Mixture: calc.	15·1	17·1	25·0	—
found	14·8	17·8	24·4	—
	15·4	16·3	24·8	—
	15·2	17·6	25·7	—
Natural gas	7·9	3·0	1·45	0·2
	7·6	2·8	1·7	0·2

Separation and analysis of gaseous Freons

The high polarity of zeolites offers fair possibilities for the separation of polar substances, e.g. halogen derivatives. The separation of some Freons is demonstrated in *Figure 5.*

Chromatographic Spectra on Substituted and Natural Zeolites

By replacing the sodium ion with other cations, it is possible to obtain new sorption properties of the zeolite.

Figure 6 shows a survey of the position of some gases in the chromatographic spectrum on various substituted or natural (New Jersey, glauconite) zeolites. It is interesting to observe the shift of position of the *iso*- and *n*-butane on sodium, silver and manganous zeolite, as well as on natural

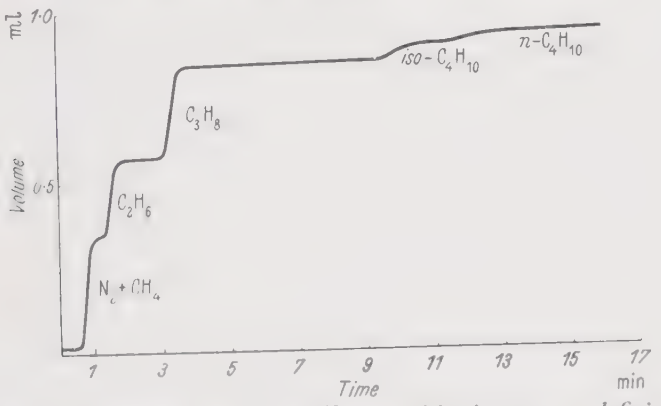

Figure 7. Chromatogram of paraffin impurities in gaseous olefinic mixture (carrier gas, carbon dioxide)

glauconite. It is seen that manganous zeolite is most convenient for the separation of both isomers. The increase of the sorption effect of silver zeolite against the olefins is noteworthy.

Estimation of small amounts of paraffins in technical olefins

The column is filled with 12 g silver zeolite of grain size 0·2–0·4 mm with 14 per cent silver content. The measured sample of 10–15 ml gas is taken up.

The impurities released by the olefins leave the chromatograph column and are simultaneously separated, as may be seen in *Figure 7*.

A long cleaning of the column (2 hours) of the olefins is a disadvantage of the process. *Table II* summarizes some of the results.

Vapour phase chromatography on zeolites when compared with the

Table II. Reproducibility of Determination of Small Quantities of Paraffins in Gaseous Olefin Mixtures

Sample ml	C_2H_6 ml	%	C_3H_8 ml	%	*iso*-C_4H_{10} ml	%	*n*-C_4H_{10} ml	%
10·10	0·102	1·02	0·260	2·57	0·050	0·49	0·101	0·99
14·35	0·145	1·10	0·366	2·55	0·072	0·50	0·150	1·05
12·25	0·130	1·06	0·328	2·60	0·055	0·45	0·135	1·10
Calc.	—	1·10	—	2·52	—	0·50	—	1·08

separation techniques of James and Martin[4] has the following advantages and disadvantages:

(*a*) It has a larger concentrating effect
(*b*) It is non-volatile and, in addition, has higher polarity
(*c*) It gives easier separation of some isomers (*n*-butene and *iso*-butene)
(*d*) It gives the possibility of separating even the permanent gases at lowered temperatures
(*e*) The elution curves, mainly on polar substances and with higher boiling materials, are not symmetrical on account of the non-linear adsorption isotherm, and
(*f*) Preparation of adsorbents with identical characteristics is difficult.

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DISCUSSION

R. M. Barrer: Perhaps I can take a moment from the Chair since the question of these crystalline molecular sieves was raised. I think Dr Janák's last point, that the preparation of absorbents of exactly identical characteristics is difficult, is quite largely met by the use of crystals which do have reproducible characteristics or can be made to have reproducible characteristics. It is also perfectly true, as a previous speaker emphasized, that the geometrical factor in absorption can now be made

quantitative. It is quite possible to take crystals which will obviously occlude a normal paraffin but will not admit a paraffin which has a branch side chain. This is not only true of the Linde sieve, the commercial material, it is true of natural and synthetic chabazites and certain other species. The rather interesting fact is that the geometrical property can be made very nearly quantitative for pairs of molecules which differ as little in dimension as oxygen and nitrogen. This is true of the Linde sieve material itself. At −180 C this material will take up practically no nitrogen at all but will freely and copiously occlude oxygen. This property is shared by levenite, calcium mordenite, synthetic or natural calcium mordenite, and in some cases—though chabazite is a somewhat more complicated system from this point of view—selectivity is introduced to chabazite by ion exchange. That is another factor mentioned by Dr Janák which can produce an extraordinarily high influence with crystalline zeolites. It is quite possible to introduce a sodium ion—say, two sodium ions in place of one calcium ion—and completely transform the absorptive characteristics of the crystal. It is as though the cation acts as sentinel, gets in the way, and stands before all the channels or windows that allow molecules to sift into the crystals. Consequently you may find that, let us say, a sodium ion will block the crystal almost completely for a given species, whereas for the calcium form it may be completely open to that same species.

I mention this not as a question to Dr Janák, but as a comment on certain of the factors which are mentioned at the end of his paper.

22

THE APPLICATION OF GAS CHROMATOGRAPHY TO ORGANIC FLUORINE CHEMISTRY

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Gas–liquid partition chromatography has been applied as a general organic technique with particular emphasis on fluorine chemistry. Analytical scale columns are used for following reactions, identification of products, assaying of purity, etc. No single packing seems to be satisfactory for general application; it is advisable to use several. Dinonyl phthalate/kieselguhr is, rather surprisingly, very useful with fluorine compounds, as are silicone rubber alone, silicone oil/silicone rubber, dinonyl phthalate/silicone rubber, and *bis*(heptafluorobutyl) phthalate/silicone rubber. Preparative scale columns have been developed for separations of 1–10 g of volatile mixtures and are now in general use. Applications of the technique to specific problems in fluorine chemistry are described.

Our interest in gas–liquid partition chromatography[1,2] has been its application to general organic chemistry, and particularly to fluorine chemistry, which is a major research interest in this department. It is a subject to which gas chromatography is an exceptionally valuable aid for several reasons. Organic fluorine compounds are volatile (often, boiling points are lower than for analogous hydrocarbon derivatives) hence the method is widely applicable. Isomeric or closely related fluoro-derivatives usually have physical properties which are very similar, rendering separation difficult. Also, azeotropes are encountered fairly frequently. Due to difficulties of synthesis, only small quantities of materials are generally available for study so that elaborate distillation techniques cannot be employed.

We have applied the gas chromatographic technique to organic fluorine chemistry in two ways. Analytical scale columns have been utilized for the control of reactions and for investigations of products, etc. Further, it was obvious to us that if the scale of the chromatographic process could be increased it would be of tremendous value preparatively. The problem of purification or separation of small quantities of volatile compounds, has been an exceedingly difficult one hitherto. The objective of preparative scale working has been achieved readily[3], and columns capable of dealing with 1–10 g of volatile mixtures are now in routine operation.

It should be emphasized that our interest in the technique is primarily in its application to organic chemistry, and not in the development of the method itself.

Description of Techniques Used

1. *Analytical scale work*

(*i*) *Apparatus*—In general, our technique follows that of Ray[2]. Thermal conductivity is used for detection, since a very high sensitivity is not essential for general organic work. Relatively large amounts of samples are usually available. Except where an impurity emerges very close to the major constituent, it is easy when testing for purity to overload the tube. Glass U-tubes are used as columns in vertical electrical heaters. The changing of tubes and variation of the temperature of the system are thereby accomplished readily. Tungsten spirals are used in the detector; they are much more robust than platinum ones and enable the cells to be more compact.

(*ii*) *Investigation of tube-packings*—As the work has proceeded numbers of organic liquids have been tested as column-packing materials (see *Table 1*). Ray's packing[2], dinonyl phthalate/kieselguhr is very useful with highly fluorinated compounds, perhaps rather surprisingly, in view of the insolubility of many of them in hydrogen-based organic substances. Though we have found a number of cases for which it gives poor separations, it is still one of our standard packings. In contrast, mixtures of kieselguhr and high-boiling fluoro-oils or fluoro-chloro-oils (in which only traces of hydrogen remain) are not particularly good packing materials. Often, separation was not achieved and even with perfluoro-compounds (containing no hydrogen) separations were in general only slightly better than those obtained with hydrogen-containing liquids.

We have found that powdered silicone rubber is a good packing material in gas chromatography. The sample used, a polymethylsiloxane gum which had been mixed with kieselguhr and vulcanized, was a somewhat rubbery solid which was ground to the particle size required. Even when used in the dry state, many useful separations were obtained. This is of interest since the organic component is not a true liquid. The separations could be improved, however, by incorporating certain liquids into the powdered rubber (it will absorb liquids readily). Dinonyl phthalate worked well; even better was a silicone oil (again an aliphatic type). The latter was preferable also because of its higher thermal stability. The optimum proportion of the silicone oil was apparently about ten per cent of the weight of the rubber, when good separations with very sharp peaks were given. Higher concentrations gave inferior resolutions of mixtures, though retention times were greater.

The silicone oil gave a less useful packing when taken up on kieselguhr itself, as did a silicone grease, whilst a polyethylene oxide fraction, on kieselguhr, was good for only one or two particular separations.

Two fluorine-containing esters were synthesized for testing. One, *bis*(*m'*-trifluoromethylbenzoyl)octafluorohexane-1 : 6-diol (prepared by R. P. Smith), gave a fairly good packing (on kieselguhr). The other, *bis*(heptafluorobutyl) phthalate, gave good packings both on kieselguhr and, more particularly, on silicone rubber.

(*iii*) *Routine operations*—For general use in fluorine chemistry no single packing so far tested is completely satisfactory. In routine work, preliminary tests are run on the following: dinonyl phthalate/kieselguhr, silicone oil/silicone rubber, and *bis*(heptafluorobutyl) phthalate/silicone rubber. In

addition, if the product is highly fluorinated it is tested on fluoro-oil/kieselguhr and if lightly fluorinated, on polyethylene glycol/kieselguhr. A reasonably effective screening is thereby achieved and further work can be done with the best column.

Analytical scale gas chromatography is of tremendous help to the organic fluorine chemist. The uses are obvious, e.g. assaying the purity of volatile compounds, establishing and controlling reaction conditions, and identifying products. Optimum conditions can be found in pilot experiments before full scale work is started. Known products can generally be identified by analytical chromatography, and chemical characterization is then easy.

2. *Preparative scale work.*

So far, virtually all our completed work has been carried out using dinonyl phthalate/kieselguhr (1:2 by weight) as the stationary phase and discussion will be confined to this system. Our columns are 16 ft long by 30 mm internal diameter and are arranged horizontally in electrical heaters[4]. One important requirement is a flash-heater on the inlet to effect the rapid vaporization of the organic mixtures. Without this, separations are not clean. This point has been stressed for analytical columns[5]. Thermal conductivity is again used for detection and the issuing components are frozen out of the nitrogen stream in liquid air traps.

The maximum charge for a column of this type depends on the properties of the volatile mixture. For a difficult separation, say of two compounds with similar characteristics and boiling points less than 1C° apart, 0·5 g might be the limit. On the other hand, with an easy separation, the column could be deliberately overloaded until the components were only just segregated; as much as 8–10 g might then be handled. An average charge is about 3 g.

Fractionations in these large columns are characterized by the excellent recoveries of material obtained. No mixed intermediate fractions are found, and with care, components can be isolated in virtually quantitative yield. Dr J. C. Robb of this department is using the technique to follow reactions by quantitative isolation of products and unchanged reactants[6]. Many azeotropes can be separated easily. Certain polyfluoro*cyclo*hexanes form azeotropes with benzene. The former are volatile, but solid even when mixed together, and a solvent is necessary for their injection into the chromatograph tube. Chromatographically, benzene is easily separable from them and is used thus.

Separations of the type described later usually take 2–4 hours to complete. It is possible sometimes to speed up the through-put rate by introducing a second batch of mixture before the first has emerged completely. For most of our work this offers little saving of time since components which come through fairly rapidly are often present. An interesting recent development[7] applicable where numbers of similar separations are required is the mechanization of large scale gas chromatographic separations.

Applications of the Technique to Specific Problems

(A) *Fluoro*cyclo*hexanes from benzene*

The fluorination of benzene with cobaltic fluoride[8] gave a mixture of polyfluoro*cyclo*hexanes. This was too complex for easy resolution by distillation

which gave only two definite fractions, undeca-(I)[8] and 1*H*:3*H*-deca-fluoro*cyclo*hexane(II)[9]. Other fractions obtained were of doubtful purity. The crude material was examined by analytical gas chromatography and the two known and three new compounds detected. In this case, by controlling the fractionation by analytical chromatography, fairly pure specimens of the latter were isolated, and characterized (see below) as 1*H*:2*H*-deca-(III), 1*H*:4*H*-deca-(IV), and 1*H*:2*H*:4*H*-nona-fluoro*cyclo*hexane(V). The chief reaction of each of these compounds is the elimination of hydrogen and fluorine from adjacent carbons to give olefins.

(B) *Reactions of* 1H:3H-*decafluoro*cyclo*hexane*(*II*)

These have been described already[3,9]. With aqueous alkali, octafluoro-*cyclo*hexa-1:4-(VI) and -1:3-diene(VII), and 4*H*-(VIII) and 3*H*-nonafluoro-*cyclo*hex-1-ene(IX), were given. The latter two were separated in the large column and characterized, using chromatography, followed by chemical identification. This problem had been insoluble without this technique.

(C) *Reactions of* 1H:2H-*decafluoro*cyclo*hexane*(*III*) (with R. P. Smith)

After treatment with aqueous potassium hydroxide, three main products, octafluoro*cyclo*hexa-1:3-diene(VII)[9], and 1*H*-(X)[10], and 3*H*-nonafluoro-*cyclo*hex-1-ene(IX)[3], and much starting material were identified chromatographically. The presence of only these three products strongly suggested the 1*H*:2*H*-structure for III. The 1*H*-olefin(X), assuming no rearrangements occur, can arise only from such a precursor.

However, a 1*H*:2*H*-decafluoro*cyclo*hexane[III(a)], with different properties (b. pt 20C° higher) had been isolated from another process[10] [C_6F_{10}(XIV) → $C_6F_{10}Cl_2$ → $C_6F_{10}H_2$]. Repetition of this and gas chromatographic examination of the product revealed the presence, not only of III(a), but also of III in smaller quantities, undetected previously in the intermediate fractions from the distillation. Because of the relative difficulty of dehydrofluorination of III and the formation of some 1:3-diene, it is believed that it is the *trans*-isomer, and III(a) the *cis* (assuming that *trans*-elimination of hydrofluoric acid is favoured).

(D) *Reactions of* 1H:4H-*decafluoro*cyclo*hexane*(*IV*) (with J. A. Godsell)

Treatment with aqueous potassium hydroxide of a specimen (purified by large scale chromatography) was followed by analytical chromatographic examination. Three products only were detected, octafluoro*cyclo*hexa-1:4-(VI), and -1:3-diene(VII)[9], and 4*H*-nonafluoro*cyclo*hex-1-ene(VIII)[3]. Large scale chromatographic isolation of these was followed by characterization by infra-red measurements and by oxidation to give the appropriate fluoro-dibasic acids[3,9]. The structure was thus established, since only the 1*H*:4*H* system (IV) gives the 4*H*-olefin exclusively as the product of elimination of 1 mol of hydrofluoric acid.

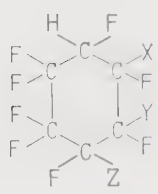
(E) *Reactions of* 1H:2H:4H-*nonafluoro*cyclo*hexane*(*V*) (with J. A. Godsell)

A structure of this type theoretically can give twelve unsaturated derivatives on dehydrofluorination. After treatment with alkali, chromatographic examination showed the presence of nine products. Large scale separation

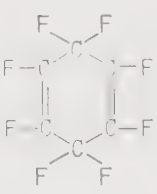
has readily given those present in largest amount (again this complex mixture would be extremely difficult to resolve otherwise). Two have been investigated further; one is either 1*H*-(XI) or 2*H*-heptafluoro*cyclo*hexa-1:3-diene (XII), the other is hexafluorobenzene(XIII), indicating the 1*H*:2*H*:4*H*-structure(V) for the starting material, since other isomers cannot give both types [(XI) or (XII), and (XIII)] together.

These problems, selected from many being pursued by the Birmingham research group, would have been extremely difficult to tackle without gas chromatography. Separations of the reaction mixtures into pure components can be done practicably only by preparative scale chromatography, and furthermore only small quantities are required. Analytical chromatographic examinations, showing the numbers of products present, and in some cases the definite absence of certain possible ones, provide vital evidence for allocations of structures.

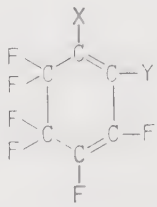
These studies on fluoro-organic compounds will be reported in more detail later.



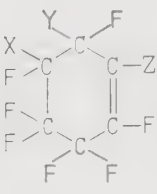
I X=Y=Z=F
II X=Z=F, Y=H
III Y=Z=F, X=H
IV X=Y=F, Z=H
V Y=F, X=Z=H



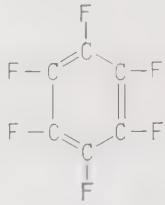
VI



VII X=Y=F
XI X=H,Y=F
XII X=F,Y=H



VIII X=H, Y=Z=F
IX Y=H, X=Z=F
X Z=H, X=Y=F
XIV X=Y=Z=F



XIII

Experimental

Apparatus

Analytical scale gas chromatography—A glass U-tube was employed (of 6 ft 6 in total length 4 mm internal diameter), one end carrying a serum cap, the other being connected directly to the detector. Nitrogen (oxygen-free), dried over silica gel, and metered through a rotameter, was introduced via a side arm joined to the tube just below the end closed by the serum cap. The U-tube was carried vertically in an electrical heater, comprising a copper tube, wrapped in asbestos paper, and then wound with an element, the entire heater being finally coated with cement. The winding was arranged to give an even temperature (within 2C°) along the entire length.

To assist vaporization of the samples a roll of nickel gauze was inserted into the side arm, which was fitted with a subsidiary tubular heater running about 50C° hotter than the main heater.

The issuing components in the gas stream were detected by thermal conductivity. The cell consisted of a cylindrical copper block ($3\frac{3}{4}$ in long 2 in diameter) at room temperature. In each of two vertical holes ($\frac{9}{32}$ inch diameter) there was carried, on a brass former suspended from a $\frac{3}{16}$ inch Whitworth bolt insulated by a 'Fluon' washer, a spiral of very fine tungsten wire. Horizontal holes bored from the sides of the block into the vertical

channels completed the circuits for passage of gas. The spirals (length 1⅜ inch, resistance 60 ohms each) carried a current of 35 mA, controlled by a baretter valve. The two spirals were incorporated in a Wheatstone bridge circuit (the other two arms being of manganin), the off-balance potential being amplified in a 3-valve a.c. amplifier (15,000:1), rectified, and passed to a recording milliammeter (Evershed and Vignoles, F.S.D. 1 mA, resistance 20,000 ohms).

The exits of the columns were at atmospheric pressure (fluoro-compounds have high vapour pressures). At flow rates of 1·5 l./h the ingoing nitrogen was about 34 cm of mercury above atmospheric pressure with most columns.

Flow rates used were generally 1·0–1·5 l./h. For difficult separations these values were rather high and better resolutions could usually be obtained at lower flow rates though peaks were then less sharp. Column temperatures were normally near the average b. pt of the test mixture. Again, better resolution though with broader peaks was possible at lower operating temperatures.

Preparative scale gas chromatography—The preparative column consisted of two parallel tubes 8 ft × 3 cm internal diameter, joined by a short section of fine-bore capillary tubing. The column was mounted horizontally in a series of electrical heaters[4]. The samples were introduced via a small burette in which the pressures could be equalized. A tape heater was wound around the column inlet. Detection was by thermal conductivity, using a less sensitive cell incorporating two straight platinum wires. Again, the exit was at atmospheric pressure, excess pressure on the inlet side being about 11 cm of mercury for a flow rate of about 6 l./h.

The fractions were collected in traps cooled by liquid oxygen, and arranged in parallel beyond the detector. The recorder trace served merely to indicate when particular fractions were to be collected. With experience, it is easy to forecast behaviour in the large column from traces given by the analytical one.

Examination of column packings

Filling of tubes—Each tube was packed with about 10 g of stationary phase. The packings were prepared by mixing the solid phase with the liquid phase and an excess of ether, and vigorously stirring the resultant slurry. The ether was evaporated off. The columns were then packed under slight suction and with gentle but continuous tapping of the tube with a glass rod. Care is necessary with this filling process; too tight a packing gives an excessive pressure drop across the column and reduced efficiency.

Packings used—The following packings were tested. Throughout, the kieselguhr used was 80–100 mesh and the silicone rubber 60–80 mesh.

(1) Dinonyl phthalate/kieselguhr (1:2 parts by weight).

(2) *bis*(Heptafluorobutyl) phthalate/kieselguhr (1:2 parts by weight).

This *ester*, b. pt 145–150°C/20 mm of mercury (Found C, 36·6; H, 1·6. $C_{26}H_8F_{14}O_4$ requires C, 36·2; H, 1·5 per cent) was prepared by treatment of 1:1-di*H*-heptafluorobutan-1-ol with phthaloyl chloride in pyridine solution.

(3) Silicone rubber crumb.

This was supplied by the Dunlop Rubber Co. A silicone rubber gum (based on a dimethyl polysiloxane) was mixed with equal parts of

kieselguhr and vulcanized with benzoyl peroxide. The product was ground mechanically in a Masson cutter.

(4) Dinonyl phthalate/silicone rubber (1:4 parts by weight).

(5) *bis*(Heptafluorobutyl) phthalate/silicone rubber (1:4 parts by weight).

(6) Silicone oil/silicone rubber (1:10 parts by weight).

(7) Silicone oil/silicone rubber (1:4 parts by weight).

(8) Silicone oil/silicone rubber (1:2 parts by weight).

(9) Silicone oil/kieselguhr (1:4 parts by weight).
The oil used in packings (6)–(9) was Silicone Fluid 703 supplied by W. Edwards and Co. (London), Ltd.

(10) Silicone oil/kieselguhr (1:4 parts by weight).
This oil (kindly given by Dr G. A. P. Tuey of May and Baker Ltd) was Rhodorsil Silicone Fluid 47–V–300, believed to be an aromatic type.

(11) Silicone grease/kieselguhr (1:2 parts by weight).
This was silicone high-vacuum grease [W. Edwards and Co. (London), Ltd].

(12) Apiezon Oil J/kieselguhr (1:4 parts by weight).

(13) Polyethylene glycol/kieselguhr (1:2 parts by weight).
This was 'Carbowax' Polyethylene Glycol 400, supplied by Gemec Chemicals Co.

(14) Fluorocarbon oil/kieselguhr (1:2 parts by weight).

(15) 2:2:3:3:4:4:5:5-Octafluorohexane-1:6-diol di(*m*-trifluoromethyl benzoate)/kieselguhr (1:2 parts by weight).

Mixtures tested—(*a*) Perfluoro*cyclo*hexa-1:4-(VI) and -1:3-diene(VII), and 4*H*-(VIII) and 3*H*-nonafluoro*cyclo*hex-1-ene(IX) (b. pt 57, 63, 69 and 70°C, respectively), obtained from 1*H*:3*H*-decafluoro*cyclo*hexane(II)[3,9].

(*b*) Undeca-(I), 1*H*:2*H*-deca-(III), 1*H*:3*H*-deca-(II), and 1*H*:2*H*:4*H*-nonafluoro*cyclo*hexane(V) and benzene(*i*) (b. pt 63, 70, 78, 92 and 80°C, respectively). I–V were prepared from benzene by fluorination with cobaltic fluoride[8]. I–III give azeotropes with benzene.

(*c*) 1:1:2-Trichloro-1:2:2-trifluoroethane(*i*), 1:1:2-trichloro-1:2-difluoroethane(*ii*), and 1:1:2:2-tetrachloro-1:2-difluoroethane(*iii*) (b. pt 47, 72 and 92°C, respectively).

(*d*) The ketones, $CF_3{\cdot}CO{\cdot}R$[11], where R = ethyl(*i*), *iso*propyl(*ii*), *tert*-butyl(*iii*), and *n*-butyl(*iv*) (b. pt 45, 58, 70 and 90°C, respectively).

(*e*) Perfluoro*cyclo*hexane(*i*), perfluoro-*neo*hexane(*ii*), and decafluoro*cyclo*hexene(XIV) (b. pt 52, 59 and 53°C).

(*f*) Diethyl ether(*i*), and isomeric dichloro-decafluoro*cyclo*hexanes[10](*ii*) (b. pt 35 and 109°C, respectively).

(*g*) Ethyl alcohol(*i*), chloroform(*ii*), and carbon tetrachloride(*iii*) (b. pt 78, 61 and 78°C, respectively).

(*h*) Products from the reaction of decafluoro*cyclo*hexene(XIV) with lithium aluminium hydride in diethyl ether. Three main components are present, b. pt (*i*), 89°C; (*ii*) 90°C and (*iii*) 113°C. A fourth (smaller) component (*iv*) has b. pt 64°C.

Table I

The results shown in the following table are, for each run, the distances (mm), measured on the recorder charts, from the start line, at which point the sample was injected, to the peak maxima. The chart speed was 12 in/h throughout. Where two values are given for a component, it has been resolved to give two peaks. The sharpness of the peaks also influences the completeness of the separations. Packings *6*, *9*, *11*, *2*, *5*, *1*, gave sharp peaks, *6* especially so.

Test mixture	*Component*	*Column packings tested*														
		1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*
(*a*)	VI	13	19	15	19	25	19	17	15	9	13	14	6	5	18	21
	VII	19	24	19	25	34	25	23	25	12	*	*	*	6	24	30
	VIII	29	30	*	34	40	26	25	28	14	16	18	*	12	*	36
	IX	38	35	*	43	47	30	30	33	16	*	*	*	15	*	*
(*b*)	I	18	24	14	22	27	19	18	18	9	12	14	6	7	19	20
	III	28	33	18	32	40	25	27	28	13	15	17	*	15	23	33
	II	59	{50 {53	22	56	{56 {60	{33 {36	{35 {38	{40 {42	21	{17 {20	{20 {22	*	43	28	53
	V	105	81	33	88	83	53	60	71	37	26	30	11	122	36	60
	i	96	33	71	122	91	113	118	153	76	55	64	51	79	13	99
(*c*)	*i*	24	15	28	36	34	40	38	44	19	23	26	12	10	11	19
	ii	111	35	57	116	79	94	96	122	62	45	50	32	48	17	57
	iii	*	43	98	150	122	155	152	184	88	77	84	57	94	25	68
(*d*)	*i*	21	16	16	23	24	22	21	25	13	13	14	5	—	10	22
	ii	27	21	23	33	36	33	31	37	19	19	20	8	—	14	81
	iii	42	33	36	54	58	82	53	59	30	29	31	12	—	22	49
	iv	81	51	54	96	91	52	85	98	52	43	45	18	—	27	31
(*e*)	*i*	7	9	9	7	13	10	8	7	4	18	—	4	4	15	7
	ii	*	*	*	*	*	*	*	*	*	*	—	*	*	*	*
	XIV	9	12	11	11	18	13	11	11	6	14	—	*	*	*	13
(*f*)	*i*	22	12	24	31	28	34	33	38	20	21	27	11	13	10	18
	ii	49	{63 {66	67	80	116	95	84	90	36	55	62	16	8	69	64
(*g*)	*i*	32	19	20	32	25	26	26	31	16	17	21	8	128	10	27
	ii	100	26	50	100	57	78	84	110	56	38	48	27	*	*	39
	iii	86	*	76	110	74	112	116	149	70	58	74	44	52	14	43
(*h*)	*i*	89	67	35	87	77	53	54	66	31	—	35	11	56	33	65
	ii	124	84	39	115	94	62	65	81	39	—	40	*	85	36	85
	iii	235	138	64	200	156	107	119	153	76	—	69	20	187	52	152
	iv	*	*	19	*	*	25	22	*	*	—	19	6	10	*	27

Working temperatures were 78°C throughout.
Nitrogen flow rates were 1·2 l./h except for packings *3* and *11* (0·5 l./h) and packings *6–8* (1·0 l./h).
* Not separated.

Application of gas chromatography to specific problems

(A) *Fluorohydrocarbons from benzene*—The mixed product[8] was a low melting solid, as were individual fractions: any unchanged benzene gave azeotropes with material having b. pt ~ 80 C. Analytical gas chromatographic investigation of the material with b. pt ~ 94 C on several packings showed only six compounds. One was perfluoro*cyclo*hexane and was removed by fractional distillation as an azeotrope (b. pt 28 C) with ether. Further distillation gave two known (I and II) and three new compounds, the former pure, the latter fairly pure. These were III, b. pt 70; IV, b. pt 86; and V, b. pt 92°C.

(B) *Reactions of 1*H*:3*H*-decafluoro*cyclo*hexane(II)*—Earlier work has been reported already[3]. On several packings (*Table I*), II gives two peaks very close together. It is believed that these are due to the presence of stereoisomers; confirmation awaits preparative scale separations on silicone columns.

(C) *Reactions of 1*H*:2*H*-decafluoro*cyclo*hexane(III)* (with R. P. Smith)—The compound (1·0 g), potassium hydroxide (1·0 g) and water (2·0 ml) were vigorously shaken in a sealed tube at 100°C for 2 hours. The product was investigated chromatographically [dinonyl phthalate/kieselguhr (1:2)] and five peaks were found. At 55°C, nitrogen flow rate 1·0 l./h, retention times were (in minutes) (i) 6·0, (ii) 9·5, (iii) 11·0, (iv) 15·0, and (v) 22·5; at 55°C, nitrogen flow rate 0·2 l./h, the times were 8·0, 14·0, 16·2, 23·0, 35·5, respectively, and the resolution was improved considerably. Peaks (i) and (v) were very small; (i) is due to an unidentified degradation product and (v) to IX. Fairly large peaks (ii) and (iv) were given by VII and by unchanged starting material (III). The largest peak (iii) was due to X.

By repetition of earlier work[10], another sample of 1*H*:2*H*-decafluoro*cyclo*hexane was prepared. Gas chromatographic examination showed two peaks, besides ether (temp. 78°C, nitrogen flow rate 1·2 l./h. Retention times 4·5 and 22 minutes). The former was coincident with that given by III, b. pt 70°C, and the latter, a much larger peak, with that from the material [III(a)] (b. pt 91°C) previously isolated from this reaction[10].

(D) *Reactions of 1*H*:4*H*-decafluoro*cyclo*hexane(IV)* (with J. A. Godsell)—The decafluoro-compound (1·5 g), purified in the large column, was boiled for 4 hours with potassium hydroxide (1·5 g) in water (7·5 ml). Examination of the product in the analytical chromatograph column (dinonyl phthalate/kieselguhr, temp. 80°C; nitrogen flow rate, 1·6 l./h) gave three peaks. The first two (after 1·4 and 2·0 minutes) were coincident with those given by authentic 1:4-(VI) and 1:3-diene(VII), respectively, the third (after 3·25 minutes) was from VIII[3].

IV (45 g) was then boiled for 4½ hours with potassium hydroxide (45 g) in water (225 ml). The organic phase (35 g) was separated and the components isolated chromatographically to give VI, b. pt 57; VII, b. pt 63; and VIII, b. pt 69°C. These were characterized spectroscopically, and by oxidation to the expected fluoro-dibasic acid, in each case. All the products were identical with authentic materials[3,9].

(E) *Reactions of 1*H*:2*H*:4*H*-nonafluoro*cyclo*hexane(V)* (with J. A. Godsell)—The compound (100 g), potassium hydroxide (100 g), and water (100 ml) were refluxed together for 4½ hours, and the product then retreated as before for 4 hours further. Analytical chromatographic examination showed nine peaks. The mixture was separated in the large column (temp. 80°C, nitrogen flow rate 9 l./h). Two of the fractions have been investigated further. One, b. pt 72·5°C, was oxidized to tetrafluoro-succinic acid[9], and is either XI or XII.

Another, b. pt 79·5–80°C, is hexafluorobenzene(XIII) as shown by analysis, spectroscopy, and the addition of chlorine, which gives a hexachloro-hexafluoro*cyclo*hexane, m. pt 101–102°C.

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23

THE CONSTRUCTION OF AN APPARATUS FOR STUDIES IN VAPOUR PHASE CHROMATOGRAPHY AT TEMPERATURES UP TO 300°C

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Monsanto Chemicals Ltd, Ruabon

An apparatus for studies in vapour phase chromatography, using the Martin gas density balance, is described in detail. The partition columns and detector are mounted in a vapour jacket, suitable for use at temperatures up to 300°C.

The use of the method in quantitative analysis is illustrated by the analysis of a mixture containing phenol, hydroxy diphenyls, and diphenyl sulphone. Accuracies approaching ± 1 per cent for each component present are obtainable.

THE results reported by various workers in the field of vapour phase chromatography during recent years suggest that, provided suitable stationary liquids are available, the technique should provide a useful method for the quantitative analysis of mixtures of organic compounds of high boiling point. An apparatus (*Figure 1*) has been constructed with this aim in view, the column and detector system being capable of operating at temperatures up to 300°C.

Essentially, the apparatus consists of a pair of partition columns, and a detector, the complete assembly being mounted in a vapour jacket for purposes of temperature control. The partition columns are connected to a source of nitrogen, and provision is made for control of the input pressure and flow rate. Samples under analysis are introduced at the inlet to one of the columns, and detection of components is effected by continuous comparison of the density of the eluate from each column, using the Martin gas density balance.

The apparatus has been operated satisfactorily at 290–295°C, using Celite 545 impregnated with Apiezon L vacuum grease [Edwards and Co. (London) Ltd] in proportion 2 : 1 by weight as the column packing. The use of fluorinated hydrocarbons and polyethylene glycols as stationary liquids at high temperature is being investigated.

EXPERIMENTAL

Construction of the apparatus

The detecting system used is a gas density balance, a detailed description of which will be found elsewhere. It is similar to that originally designed by A. J. P. Martin, and is a means by which the density of a moving column of gas can be continuously compared with the density of a similar column of

reference gas. An anemometer cell is arranged such that a density differential gives rise to a flow of the reference gas over a heated differential thermocouple, the output of which can be suitably amplified and recorded. Gas throttling rods are provided to balance the system such that it is insensitive to gas flow, the thermocouple output remaining at zero for zero density differential.

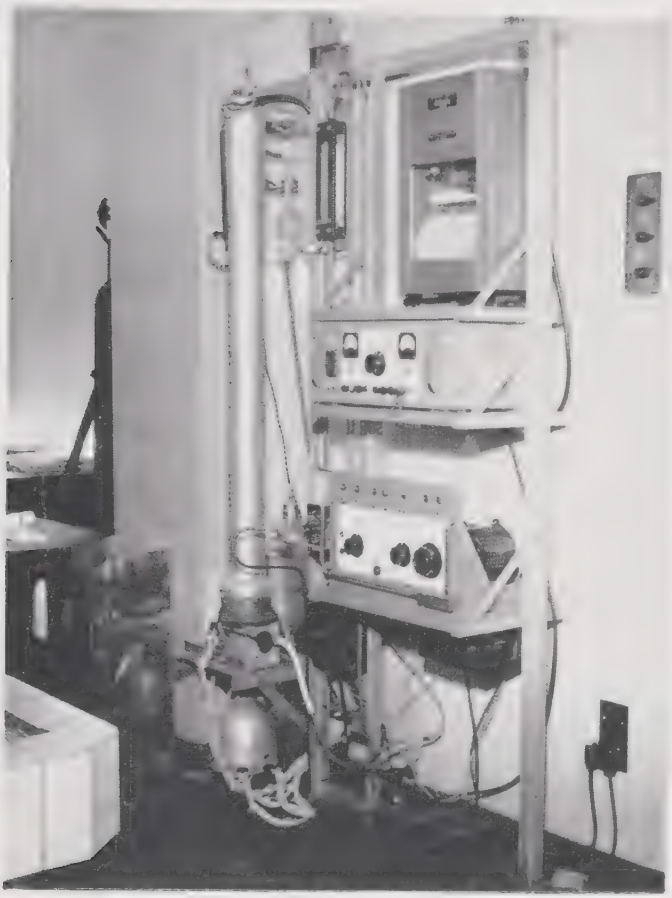


Figure 1. Complete apparatus

Connection of the detector to the pair of partition columns, and its mounting within the vapour jacket assembly is illustrated in *Figures 2–4*. Copper connector bushes are brazed on to the deoxidized copper block, which is drilled to form the density balance, with silver brazing alloy. Such bushes are provided for the thermocouple mountings C, the thermocouple heater mounting D, and the two lower throttle rods A. The two upper throttle rods are connected through a copper flange which is brazed on to the top face of the copper block. The detector is mounted in a vapour jacket formed of $\frac{1}{8}$ inch copper sheet, and is held in position by means of lock nuts threaded to the connector bushes, graphite-impregnated asbestos gaskets providing vapour-tight seals. This gasket material ('Graphitol', James Walker Ltd) has been found to be reasonably satisfactory in use with high boiling solvents at temperatures up to 300°C.

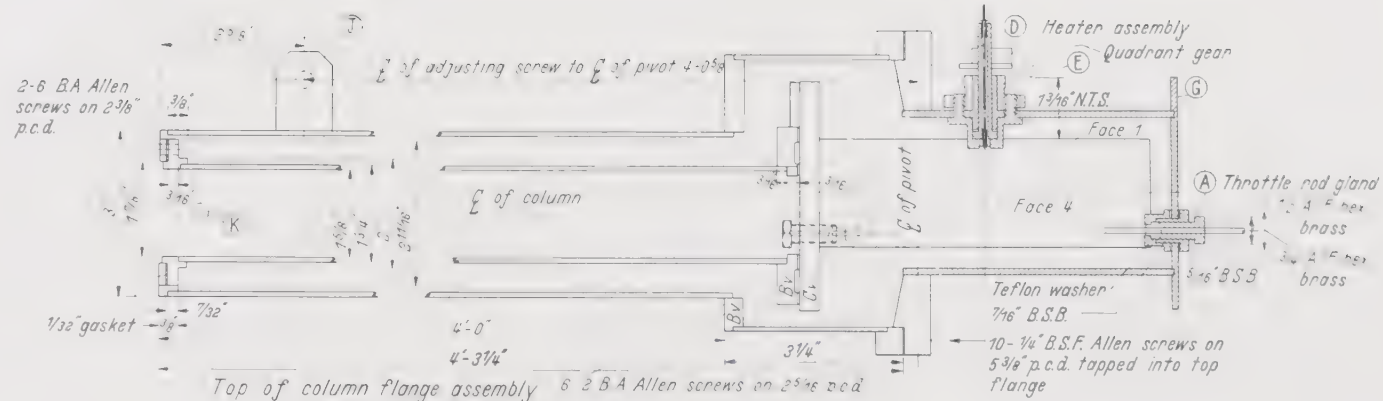


Figure 2

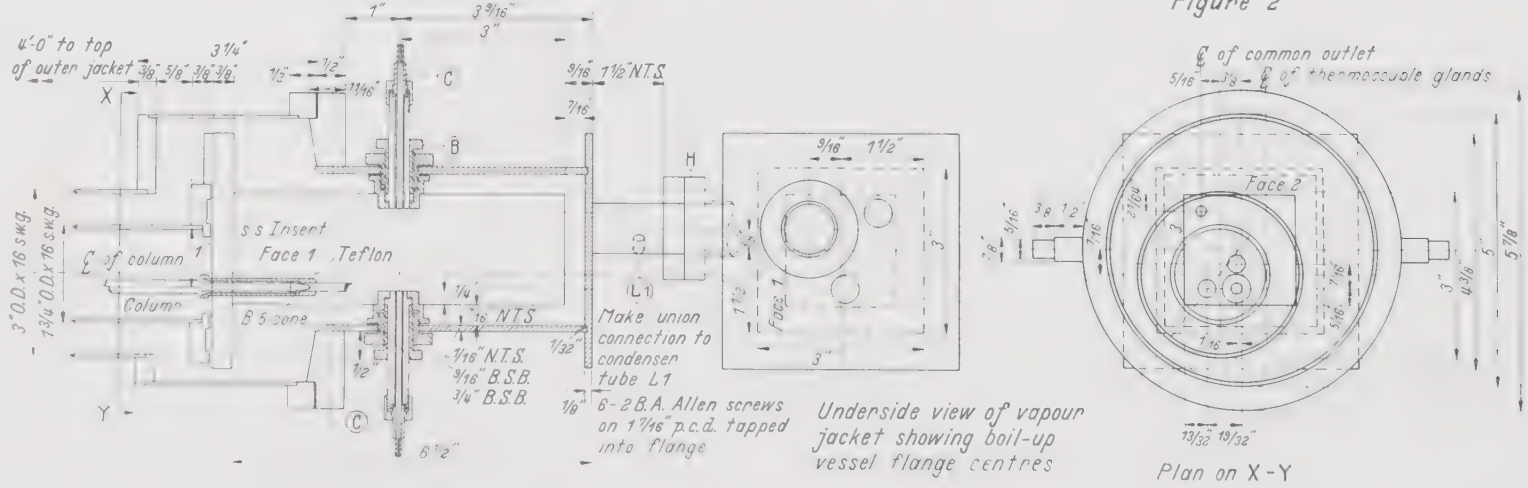


Figure 3

The heater mounting is formed from a drilled stainless steel rod having a flanged stem (*Figure 4*). Electrical connection to one end of the heater wire is effected with a length of borated copper wire, which, with application of heat, can be cemented in a soda glass tube. The glass insulated wire is then cemented to copper end plugs which are a force fit in the ends of the drilled stainless steel rod, using silver chloride. The other end of the heater wire (1 inch, 36 s.w.g. Nichrome), is earthed to a copper end plug. The heater mounting is fixed in the connector bush by means of a gland bush, which bears on the flanged stem of the mounting, and a gland nut. Rotation of the stainless steel rod for balancing purposes is facilitated by interposing a spring steel skid washer between the connector bush facing and one face of the flanged stem, and a contained Teflon washer between the gland bush and the other face of the flanged stem. The heater rod also carries a quadrant gear which is in mesh with a differential pitch lead screw. This system gives fine control of the balance position of the heater when operating the system at up to one tenth maximum sensitivity, and semi-fine control at maximum sensitivity. It also enables adjustment to be carried out at high temperature during operation.

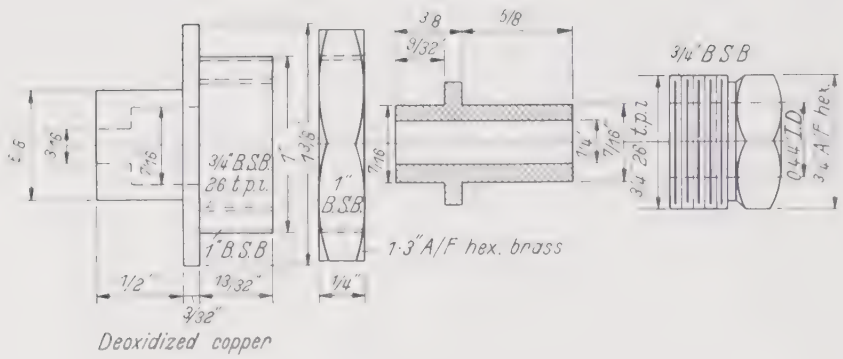
The thermocouple mountings consist of glass-lined copper tubes, flanged at one end, and held in the connector bushes by means of gland nuts, as indicated. Copper end nipples are insulated from the copper tubes with mica or Teflon washers, and are held in position by Tufnol asp gland nuts, threaded to the copper tubes. The thermocouple is threaded through its mountings, and can be viewed through the heater connector bush with the aid of a pea-lamp and travelling microscope. Accurate centring of the thermocouple in the anemometer cell is effected with a small winch and pulley assembly.

The throttle rods are fixed in position by means of gland nuts which bear on contained Teflon washers. These enable the throttle rods to be adjusted whilst keeping the system leak-proof. One throttle rod, which emerges from the density balance block into the vapour jacket space surrounding the partition columns can be pre-set and blanked off.

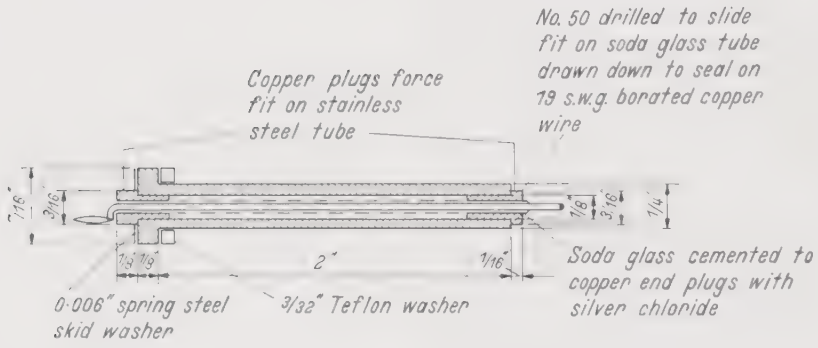
The method of connecting the sample and reference partition columns to the density balance is indicated in *Figure 3*. Stainless steel inserts are made a tight fit in the drilled entrance holes to the balance. These trap shaped Teflon washers, into which sit B5 cones connected to the outlet ends of the partition columns, to give vapour-tight joints.

The vapour jacket housing the partition columns is formed from 4 ft lengths of 3 inch and $1\frac{3}{4}$ inch diameter brass tubing, fitted with flanges, as indicated. The inner tube is fitted to the flange on the top face of the density balance block, using 'Graphitol' as the gasket material, and the outer tube carries an expansion piece with a flange to fit the vapour jacket surrounding the density balance. This method of construction enables the surface areas giving rise to direct heat loss from the balance to be reduced to a minimum, an important point when operating at high temperature. The vapour jacket surrounding the detector is thoroughly lagged to ensure an even temperature and protection from draughts. Electrical heating of the vapour jacket surrounding the partition columns assists temperature control, and is provided by two 500 W coils.

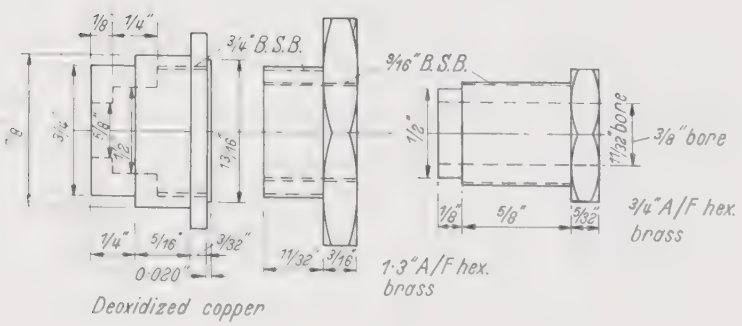
The inlets to the partition columns are fitted with B7 sockets for connection



(a)

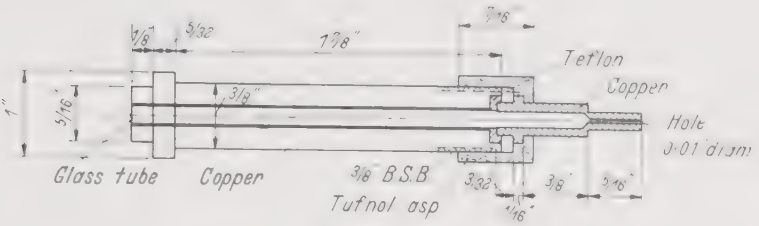


(b)

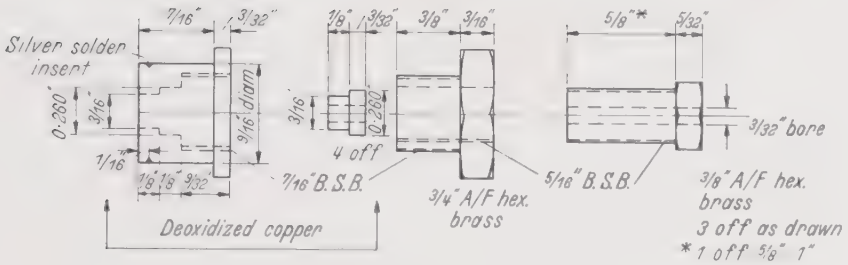


(c)

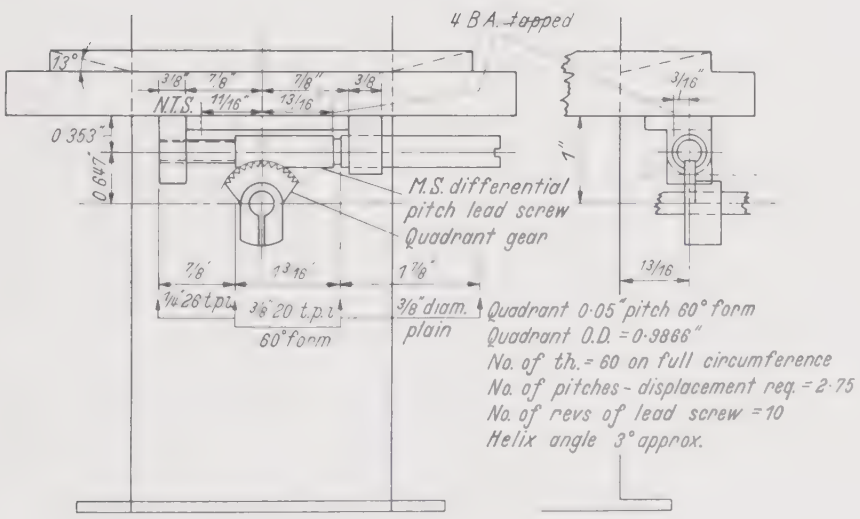
Figure 4. (a) *Heater holder gland.* (b) *Heater assembly.* (c) *Thermocouple holder gland.*



(d)



(e)



(f)

Figure 4. (d) *Thermocouple mounting.* (e) *Throttle rod gland.* (f) *Heater fine adjusting mechanism*

to the metered nitrogen supply. Sample addition at the inlet to the sample partition column, without loss of the more volatile components, is effected with a capillary mounted on a B7 cone which is connected via a stopcock to a B7 socket. The nitrogen flow is interrupted, the capillary charged with sample interposed between the column inlet and nitrogen supply line, and the nitrogen flow restarted by opening the stopcock. A small subsidiary heater aids rapid volatilization of the sample before restarting the nitrogen flow.

Results

A typical chromatogram of a mixture containing phenol, hydroxy diphenyls, and diphenyl sulphone is reproduced in *Figure 5*. 2:4:6-Trimethyl phenol is

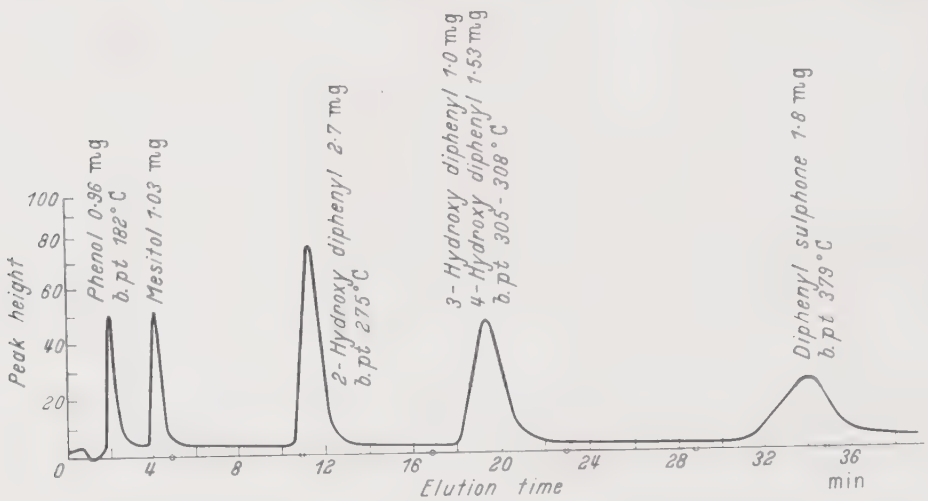


Figure 5. Typical chromatogram

Column temp. 292°C
Nitrogen flow rate 18 cm^3/min
Input pressure 55 cm Hg
Heater current 1·7 A
Amplifier gain 1/10th max.

included in this mixture as an internal reference standard for calibration purposes. This chromatogram was recorded using a detector thermocouple heater current of 1·7 A and a thermocouple amplifier gain of one tenth maximum when using the Sunvic DCA 1, MK II, d.c. amplifier. A twenty-fold increase of sensitivity can be obtained by increasing the heater current and operating the amplifier at maximum gain.

The internal reference standard calibration plot is illustrated in *Figure 6*. This was obtained by direct weighing of samples of trimethyl phenol, loaded in a capillary, before introduction to the column. The calibration plot of *Figure 7* was obtained from chromatograms of test mixtures containing known amounts of trimethyl phenol. The amount of each component present in a chromatogram was calculated from the trimethyl phenol peak height and the known concentration of the component in the test mixture.

The analysis of a test mixture of known composition, using this calibration, is indicated in *Table I*.

Conclusion

It is found that the Martin gas density balance is very satisfactory in use up to temperatures of the order 300 C, provided the vapour jacket surrounding this balance is adequately lagged. Difficulties are encountered, however, in

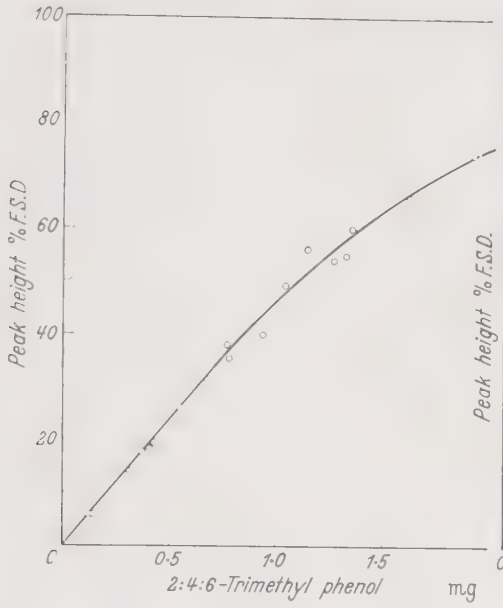


Figure 6. Calibration curve

Column temp. 290–292°C
Nitrogen flow rate 18 cm^3/min
Input pressure 50 cm Hg

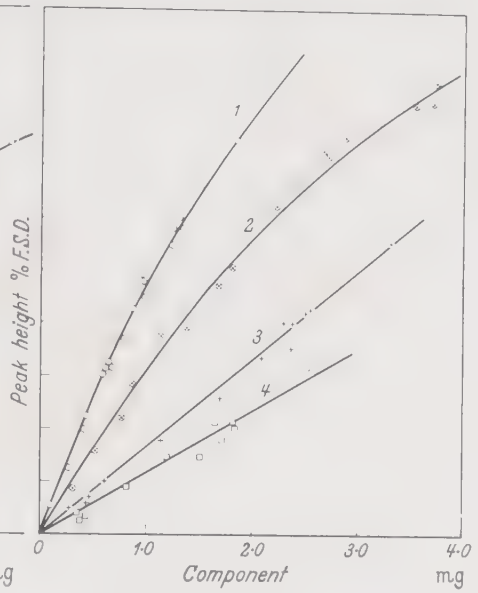


Figure 7. Calibration curves

1 Phenol
2 2-Hydroxy diphenyl
3 3- and 4-Hydroxy diphenyl
4 Diphenyl sulphone

Table I

Composition of test mixture per cent	*Analytical results*								
		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Phenol	12·0	12·7	13·0	11·8	11·4	12·6	12·6	12·0	11·9	12·8
2-Hydroxy diphenyl	33·7	34·8	35·7	34·7	35·0	35·1	35·4	33·0	34·8	33·5
3- and 4-Hydroxy diphenyls (total)	31·6	30·5	31·8	29·7	30·4	32·0	31·9	29·9	33·1	31·8
Diphenyl sulphone	22·7	22·0	22·9	21·6	21·2	21·6	24·0	20·8	24·9	20·3

Constituent	*Maximum deviation*	*Minimum deviation*	*Mean deviation*
Phenol	1·0	−0·6	0·3
2-Hydroxy diphenyl	2·0	−0·7	1·0
3- and 4-Hydroxy diphenyls	1·5	−1·7	0·4
Diphenyl sulphone	2·2	−2·4	0·6

finding suitable materials for gaskets at temperatures above 250 C. Graphite-impregnated asbestos is fairly satisfactory in use, but tends to become brittle. Difficulty is also encountered in finding suitable materials, stable enough for use in the vapour jacket. Dimethyl phthalate has been used to give a vapour jacket temperature of 290–295 C, but this material slowly decomposes, and is satisfactory only if it is allowed to bleed off slowly at the condenser. The use of controlled electrical heating in place of the vapour jacket would probably be an advantage, and an instrument is being designed with this aim in view.

So far, Apiezon L vacuum grease is the only suitable stationary liquid used at high temperature. The use of polyethylene glycols and fluorinated hydrocarbons is being investigated.

DISCUSSION

A. KWANTES: We use GLPC in three different ways, first as a self-supporting tool of analysis; secondly as a tool for collecting physical data on solution behaviour; and thirdly as a separating device for collecting fractions for further analytical work.

On the latter point, in our work we introduce into a column a known weight of sample, say about one gramme, and at the exit of the column we condense out the fraction that we want. We start it at a low temperature, about 40 C, and the temperature is increased as the analysis goes on. In this way we are able to handle C_5 up to C_{11} saturated hydrocarbon fractions in one analysis, and we can split this wide range into single carbon atom fractions and weigh these fractions to obtain the product distribution in per cent weight.

In connection with this we have to use very stable solvents, i.e. with very low volatilities, say of the order of 1 mg evolved per litre carrier gas at working temperature, otherwise we will have a gain in weight and the collected fractions would then contain contaminants.

Can you inform me on the performance of Apiezon L at temperatures of 250 or 300 C with respect to stability, for we have found that even silicone oils, for instance 703, are unstable in this respect when working at temperatures above, say, 180 C?

J. C. HAWKES: I cannot really answer that. We have not used a preparative column at high temperatures as yet. We are only now experimenting with a preparative column. It has just been completed and we are trying it with ordinary solvents at room temperature. As regards vacuum grease at 300 C, we have used the column packed with Apiezon L for a considerable period. If you add all the continuous eight-hour working days together it has probably been working continuously for something like two months now, and there has not been much change in the actual operation of the column. That is using Apiezon L on Celite at the ratio of 1 : 2. But actually how much is coming off I would not like to say. It certainly seems to be quite stable.

A. KWANTES: On this point, when you have no data actually available, do you have available strip chart papers so you can measure your retention volume as an indication of the stripping-off of this material?

J. C. HAWKES: We have not really bothered a great deal with the actual retention volumes. That particular analysis I indicated in the diagram, the hydroxydiphenyl and diphenylsulphone analysis, was carried out not quite as indicated there on peak height but on peak areas. If there has been any change in retention volume it has certainly not had any effect on the peak areas. Prior to any analysis we normally should have put in a test mixture and periodically checked that we were all right. I could not categorically state as to whether the retention volume has changed or not over the fairly long period of use of the column; I do not think it has.

H. Boer: When employing a vapour jacket at such high temperatures difficulties are encountered owing to the decomposition of the boiler liquids used. I should like to draw your attention to another method of column thermostatting that is fairly simple and gives surprisingly good results. In this method the column is heated in an air jacket, which consists of an iron tube (about 1 metre long and 4 cm internal diameter) wound with properly spaced Nichrome ribbon, and thermally insulated by wrapping asbestos cord (2 cm diameter) around it. The heater is connected to a 40–50 V stepdown transformer fed by a Variac. The Variac is connected to an Advance constant-voltage transformer. The rating of the latter has to be appreciably higher than the maximum power consumption of the jacket. In our case these details are 1 kVA and approximately 1/3 kVA respectively. Constancy of temperature has been found to be *ca.* ±0·5 C°.

G. A. P. Tuey: There are just a couple of points I want to make in connection with the use of stationary phases suitable for high temperature work. We have been engaged, like Dr Hawkes, in examining phenols, trichlorophenol, and so on, and we find that the Apiezon greases do not give the most suitable results. Silicone is more promising, and we have a sample of continental origin which is better for the purpose than anything we have tried of English manufacture. It is a commercial product. The point about this silicone is that while retention times are quite small good separation is achieved presumably by difference in the polar properties of the molecules of phenols differing only very slightly in structure. In using this silicone we have observed a phenomenon which has not been referred to here yet, that the change in retention of the column packing is not connected with the loss of stationary phase or with a change in its chemical properties. In the course of perhaps the first eight hours or so of operation of the column the retention times and column efficiency drop by about 30 or 40 per cent to a value where, in the case of chlorocresol, at about 200 C one can get column efficiencies of the order of 1000 theoretical plates as compared with perhaps 1500 at the beginning. Having reached this new and lower value the column is then apparently quite constant for an indefinite period. I feel myself that there must be some re-distribution of stationary phase on the Celite. Most careful weighing shows there is in fact no measurable loss of stationary phase, and samples of the material, the silcone oil, heated with Celite in a test tube inside the same jacket of the column show no change in physical properties over an extended period.

L. Blom: Concerning the question of Dr Kwantes on Apiezon L grease, I can tell him that I tried this at 200 C for preparative purposes. It has been shown that at this temperature more than 0·1 mg of hydrocarbon leaves the column in one minute, so that I could not use it. Much better is the silicone grease pre-treated by the method of Cropper and Heywood. I have a column at 200 C, which has worked now for more than a year, always at that temperature with the gas stream flowing, and it works very well.

W. A. Wiseman: We found that using Apiezon L, when the Celite is freshly impregnated with grease it is quite yellow in colour. After being used for some considerable time between 170 and 200 C it steadily darkens, although there does not seem to be any change in its gas-chromatographic properties. I wondered whether anybody else had come across this or whether there was any explanation for it.

J. C. Hawkes: We find exactly the same thing. It does go quite a dark brown in colour, particularly when operating at still higher temperatures, but it does not seem to impair the efficiency of the material. We mix the Celite and the Apiezon L vacuum grease at quite a high temperature and pack the columns at elevated temperatures too. That may have a bearing on it; I do not know.

G. Dijkstra: I should like to make one remark about the use of silicone grease. In the first place during the first eight hours on a total load of about 3 g about 50 mg comes off. In the second place, no two batches of silicone grease seem to be alike.

The best one we had was a very old batch which was just lying about in the laboratory, and we have never been able to obtain this same thing again, or to get any information from the manufacturers. Actually the old one gave very sharp separations and we would like to have it again but nobody can supply it. There is even a theory that the old one was adulterated with something else because at that time the silicones were just coming on to the market. I do not know what it is, but even now it is impossible to get two identical fractions from two different batches.

C. M. DREW: We have not worked with very high temperatures, but we have some interest in this since we may get to it later. This question of the darkening of the stationary phase interests me at the present time. I would like to ask Dr Hawkes, and others who have worked with these columns at high temperatures and experienced these changes that seem to be worrying us, whether or not they follow up their fraction recovery with a trap low enough in temperature to collect all the fractions of hydrocarbon that might be coming out? If so, whether or not they found a light molecule down in the C_1–C_4 class? The reason for this question is that I am concerned whether or not this darkening is due to the breakdown of the stationary phase in such a way that we get a carbon residue scattered through the packing causing a darkening, or whether it is polymerization producing such dark columns.

N. H. RAY: Although I have not had any experience of running columns at high temperatures I have done a little work on the oxidation of polymeric hydrocarbons including polythene. It would be a sufficient explanation for the darkening of the stationary phases if there were but five parts per million of oxygen in the carrier gas at these temperatures. I am not saying that that is the explanation, but it is a possible one. The oxidation proceeds under these conditions to form first peroxides which subsequently break down further into ketones.

C. M. DREW: Mr Ray, I gather that you find ketones in the exit stream of this column?

N. H. RAY: I prefaced my remarks by saying I had had no experience of using a column at high temperature, and was merely recalling some history on oxidation of hydrocarbons, quite apart from their use in columns.

C. M. DREW: I was not trying to pin you down. When we worked with columns at what I consider high temperatures (150 C), we seemed to get some aromatics coming over, the stationary phase in this case being paraffin oil. I do not know the chemical structure of paraffin oil, I presume it is a saturated hydrocarbon, it may be more or less a straight chain. But it is rather hard to understand where these aromatics come from. I do not think we had introduced them to the column previously.

G. DIJKSTRA: Our experience when running these columns at high temperatures is that if you are not very careful in purification of the nitrogen (you actually have to get out all the oxygen) you find oxidation products containing keto groups. We did not identify the substances because the mixture was very complex, but there were probably ketones present since CO groups were detected by infra-red. At present we remove all water and also the oxygen from any nitrogen we use even if it is said to be free of oxygen. This oxidation effect occurs with Apiezon greases, with polythene, and probably also with silicone grease.

GENERAL DISCUSSION

Questions were then invited on any point relating to Chapters 18–23.

J. Clifford: This is not a question about these six papers but about one in Session 3. I want to make a few general remarks about the microflame method of detecting. I think it is a wonderful example of a method which has been evolved into a very useful analytical tool in spite of the fact that the basis of the method is completely misunderstood, because it is my opinion—I feel almost certain about it—that what you are measuring in this microflame method, whatever it is it is certainly not a change in the flame temperature. I feel that this method is so good in practice it might be as well to leave well alone, but now Mr Scott is introducing these thermometric properties of heat of combustion in his calculations I feel something should be said about this. So if I may I would like to say something about flames.

You have a flame burning at the top of a tube. You have a thermocouple over the top of it. When you have a flame there is a zone of reaction which propagates itself against the flow of hydrogen, and the factors which control the size and shape of the flame are these: first of all there is gas blown up the tube; secondly, the flame is burning inwards, and the rate at which it burns inwards in a hydrogen flame is controlled by several factors which include the flame temperature, the rate at which the reaction intermediates diffuse back to the unburnt gas, and the rate at which oxygen can diffuse into the flame. This is of course hindered by the products of combustion.

When you have the hydrogen–nitrogen mixture flame at a state of equilibrium the rate of burning of the flame exactly balances the rate of supply of gas. But when you have some of these elusive substances coming in, it is observed that the flame gets much larger and engulfs the thermocouple. Why should it do this? If the effect is simply to increase the burning velocity of the mixture the flame would in fact get smaller, because the burning velocity is equal to the velocity of the unburnt gas divided by the area of the flame. If the effect is purely a thermal one the flame would get smaller, but it gets bigger. For this, it seems to me, there can be two main reasons. One is that the substances being eluted mop up the particles diffusing back from the flame fountain to prevent the flame being propagated. Secondly, the carbon dioxide helps to prevent the oxygen diffusing into the flame. Consequently these two facts completely counteract the heat effect, so the flame in effect increases in size. What you are really observing is a decrease in burning velocity of the mixture and not an increase in flame temperature. When this flame rises and engulfs the thermocouple you have a complicated state of affairs with the thermocouple. As long as the flame is below the thermocouple what it is measuring is the temperature of the hot products of the combustion. But once the flame is round the thermocouple it is not measuring a self-respecting temperature because it is itself a catalyst. You never measure flame temperature by a bare thermocouple. You get results which are completely incorrect. So whatever you are measuring it is certainly not a flame temperature. It is possible to calculate thermometrically what the temperature of a flame should be. You can calculate what the temperature of the hydrogen flame should be and what the effect on it of these small quantities of material should be. I have not done the calculation myself, it takes about a week, but you find that the kind of effect would be much smaller than would be likely to be measured by a thermocouple in that way. So I feel that Mr Scott's use of heats of combustion is quite unjustified in this connection, and the whole idea of the effect due to increase in flame temperature is quite wrong.

A. F. Williams: We have found that 'stepping' on high-speed Brown Recorders can be very annoying when it is necessary to analyse samples for the determination

of a very small impurity in a major component, the retention time of the minor component being very close to that of the major component. The difficulty has been overcome by adjusting the 'gain' and 'damping' controls on the recorder so that the pen is hunting over the smallest span to which it is adjustable. The trace will of course be slightly thicker. It is now possible to make an accurate measurement of the small peak height involved.

R. M. BARRER: Does Mr Scott want to say anything?

R. P. W. SCOTT: First I must admit I was rather surprised at this effect of calorific value on the quantitative results. On page 142 I have chosen two mixtures containing substances of widely differing calorific values. You will see on page 143 that these calorific values vary from 1–10. Now if you can correct peak areas with these values to the extent that quantitative results within 1 or 2 per cent are obtained, then the calorific values must enter into the characteristics of the detector.

That is not the only series of results. We have used three very varied mixtures with considerably varying calorific values. Although I would not like to be too dogmatic about the measurement of the flame temperature (I have not done a lot of work on such measurements), I do not think these results can be denied. The problem of deciding whether it is actually temperature or flame elongation that is effective is difficult to assess, but we normally, as I stated this morning, place the thermocouple 3·5 mm from the jet. With a flow of carrier gas of 30 c.c./min the tip of the flame does not quite reach the thermocouple. When a substance is eluted, using 1 or 2 mg of a sample which has a large number of components, you find by observation that the elongation under these circumstances is very small, but the quantitative results obviously still hold.

A. KWANTES: In connection with the discussions on sensitivities of katharometers it is probably worth while to give some details we have found in studies concerning katharometers (see table). We applied the formula as given on page 170. The component we used was *n*-pentane.

Factors affecting Katharometer Sensitivity

Wire material and diameter μ	*Nominal resistance per wire from temp.* ohm	mA *per wire*	*Reference resistance in Wheatstone bridge per arm* ohm	*Sensitivity (arbitrary units)*	
				Carrier gas	
				Hydrogen	*Nitrogen*
Pt 20	30	50	30	10	15
Pt 20	30	100	30	75	70
Pt 20	30	50	300	20	28
W 5·6	240	25	300	75	70
W 5·6	240	50	300	800	—

Katharometer block temperature 30°C

In connection with this I want to draw attention to the top line where for hydrogen a lower sensitivity was obtained than for nitrogen due to the lower wire temperature. By increasing the voltage drop twofold over the wire the sensitivity increases for hydrogen about 7·5 times and only 5 times for nitrogen. So in the comparison of sensitivities of katharometers we have to distinguish two main effects: (*1*) wire temperatures; (*2*) voltage drop over the wire, and in my opinion most workers vary these two at the same time and so the confusion starts. It is also clear that

the use of high resistances in the fixed arms of the bridge gives rise to enhanced sensitivity.

C. H. Bosanquet: Before the subject is lost altogether could I put in a word in favour of calorific values. I think what may be happening is this, that there is a fairly rough but not too bad correlation between the amount of oxygen you need to burn the sample and the calorific value. So many millilitres of oxygen produce so many calories. It will be a reasonable correlation, and therefore the more potential calories the exit gas has the more oxygen is required, and the bigger the flame area necessary for it to diffuse in. So possibly the flame volume, or something of that nature, will vary reasonably well with the calorific value. If the top of the flame only moves up a little, not getting to the thermocouple, then with a small enough movement the effect will be nearly linear. But I think there is more than pure chance in the parallelism between calorific value and integrated response.

A. J. P. Martin: It seems to me that we do not need to consider what is the flame temperature at all. In fact the combustion is over before you start measuring temperatures. In this case if the convection currents are not altered to any appreciable degree it is reasonable to suppose that the temperature at the centre of the part above the flame will be proportional to the amount of heat released in that region. Therefore Mr Scott's results are the ones I expected. I remember arguing with him when I suspected that because of the different position of the thermocouple he was not getting precisely this relationship.

M. M. Wirth: I would thank Dr Martin for making that point. We do not pretend to measure the flame temperature but merely the heat involved with the combustion. On the second point Mr Bosanquet mentioned, it might be proportional to the amount of oxygen being consumed; that was our own first impression, and the correlation with that value is very much worse than with the calorific value.

J. Clifford: I quite agree with Dr Martin as long as the flame does not actually touch the thermocouple. It is reasonable to suppose, I believe, that that is how it works, but in Mr Scott's paper he says it engulfs the thermocouple. That is what I could not understand at all because, as I say, when the flame is actually engulfing the thermocouple you are not measuring the temperature at all.

B. P. L. Weedon: We have been using an apparatus and technique modelled upon the ones which are to be described later by Cropper and Heywood, for the analysis of mixtures of fatty acids both of synthetic products and of those of natural origin. Earlier this afternoon Dr James very rightly drew attention to some of the dangers associated with carrying out too-rapid analyses of some of these complex mixtures, and I should just like to add one further word of warning. When one has a complex mixture, both saturated and unsaturated acids, then it is often highly desirable to modify the unsaturated acids first. Ozonolysis is one of those standard techniques which has just been re-investigated by these new methods of vapour phase chromatography, and we have been surprised to find the extent to which secondary reactions can take place in these decompositions. Some of the techniques recommended in the literature in the last few years can give rise to as much as 30 per cent secondary reaction products. If you are careful, and with good conditions, you can cut these down to 3 or 5 per cent, but they are still there. Obviously this does not matter at all if you are just studying the structure of pure organic compounds, but the point I want to make is that obviously you have to be rather cautious when you are trying to reconstruct the composition of a complex mixture of unsaturated acids by putting together the analytical results obtained by vapour phase chromatography of derived products.

B. T. Whitham: I would like to draw attention to the last paragraph on page 198 of my paper. We have found trace contamination of fractions with benzene after operation of silicone M.S. 550 columns for some time. We believe this is due to decomposition of the silicone fluid at temperatures above 150°C.

I would also like to agree with a number of other speakers that silicone high-vacuum grease is more satisfactory than Apiezon L at temperatures of 250 C and over. In fact we have been operating a column with high-vacuum silicone grease for about four months and there has been no change in the resolution over that period of the compounds we have been analysing.

J. BROOKS: Could I draw your attention to the footnote on page 319. Personally I have not used this particular phase, but I am sure Mr Heywood could say something about the use of this in reference to silicone greases.

24

APPARATUS FOR VAPOUR PHASE CHROMATOGRAPHY WITH ANCILLARY UNIT FOR THE DETERMINATION OF *ISO*PROPYL NITRATE IN HEAVY OILS

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An apparatus for vapour phase chromatography based on the use of glass thermal conductivity cells has been designed for operation over a range of closely controlled temperatures. The chromatograph tube and conductivity cells are housed in a single metal unit and are readily heated to a uniform temperature by the vapour from a boiling solvent. The construction of the katharometer is discussed and some of the factors which affect the sensitivity and stability of the glass cells have been investigated.

A method has been developed for the determination of *iso*propyl nitrate which is incorporated in heavy oils as an improver. An ancillary unit is attached to the head of the column and prevents contamination of the adsorbent filling by heavy fractions of oil.

When work on vapour phase chromatography began in this laboratory in early 1954 preliminary investigations were made with electrically heated columns and thermal conductivity cells housed in a metal block as employed in the work carried out in Billingham Division of I.C.I. Ltd[1].

It was realized that the applications of the chromatographic technique would be considerably extended by using heated thermal conductivity cells (katharometers). In view of the difficulties which might be encountered in designing a column and katharometer which could be uniformly heated to a specific temperature by electrical means, further work was carried out with the aim of producing an apparatus in which the column and katharometer were heated by vapour from a boiling solvent[2]. Owing to the possibility that it would be necessary to analyse vapours which might be corrosive towards metals it was decided to design the apparatus with the inclusion of glass katharometers for detection of the eluted fractions. The final design of the apparatus was such that the column and katharometer were housed in a single unit (see *Figure 1*) thus ensuring that they were heated to the same temperature. One column could be readily exchanged for another.

In order to ensure temperature stability, the katharometer arms are housed in a metal block which is directly heated by the vapour from the boiling solvent which also in turn heats the air jacket which houses the chromatograph tubes. Two columns are employed in this apparatus; the test column is

connected to the working arm of the katharometer and a 'blank' column is connected to the reference arm.

Considerable difficulties have been encountered in obtaining a stable 'zero' line at different temperatures of operation and some of these difficulties and the methods by which they have been overcome are described in this chapter.

Apart from its general use in vapour phase separations, the apparatus has been adapted to the determination of *iso*propyl nitrate which is added to fuel oil as an improver. This entails the use of an ancillary apparatus in which the *iso*propyl nitrate is expelled from the oil without serious contamination of the chromatograph column of dinonyl phthalate by fractions of the oil. *iso*Propyl nitrate present in amounts down to 0·25 per cent has been determined with a reasonable degree of accuracy. The method furnishes an example of the determination of a volatile substance in a relatively non-volatile material.

Experimental

1. Apparatus

(*a*) *Column and katharometer assembly*—The essential features and parts of the apparatus finally constructed are shown in *Figures 1* and *2*. The assembly

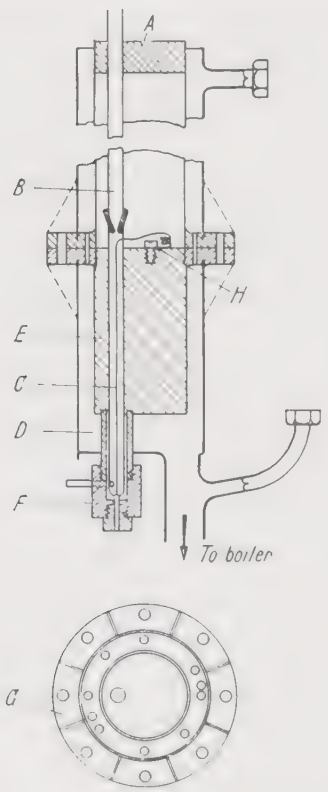

Figure 1. Column and katharometer unit

A Tufnol plug
B Analysis arm
C Katharometer
D Vapour jacket
E Metal block
F Metal seal and 'take-off' (see Figure 4)
G Top and bottom flanges
H Earthing screw

comprises a copper vapour jacket (length 4 ft) which surrounds the columns and is connected by a flange joint to a shorter jacket which surrounds a brass block which contains the working and reference arms of the katharometer. Only one arm is shown in *Figure 1*. The analysis column is connected to the working arm of the katharometer and a 'blank' column is connected to

the reference arm. Connections between the columns and katharometers are made with narrow silicone rubber valve tubing. Such a joint[3] is readily made and broken and it is a simple matter to introduce an alternative column. Silicone rubber withstands temperatures exceeding 250° C. The test arm and reference arm of the katharometer have separate nitrogen streams. This was considered better practice than passing the nitrogen stream to the test column first through the reference arm, particularly as the sample for analysis was usually added to the test column by interrupting the nitrogen stream[2].

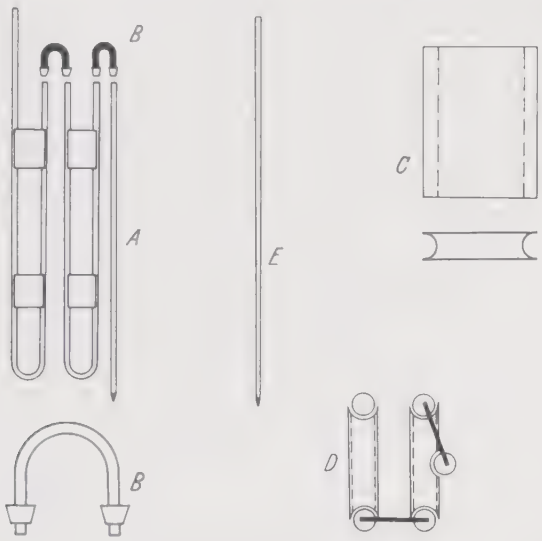

Figure 2. Glass column assembly

A Glass column of 4 mm bore
B Stainless steel capillary tubes for connecting columns
C Cork spacers for U-tube
D Plan of relative positioning
E Reference arm

The base of the vapour jacket surrounding the metal block is connected to a 2-litre copper boiler which contains the appropriate solvent which heats the column by boiling under reflux.

(*b*) *Katharometer*—A katharometer arm is shown in detail in *Figure 3*. It consists of a glass tube 2·8 mm in diameter down the centre of which a fine platinum wire of length 10 cm is suspended. A suitable gauge of wire was found to be 49 s.w.g. This wire is joined to thicker platinum wires (0·5 mm diameter) which lead to the connections to the bridge and recorder.

The joints are made by inserting the fine wire into concentric holes which are drilled in the thick wires, good electrical contact is then made by squeezing the wires together. This avoids the necessity for using soldered joints. After making the upper glass seal to the thick platinum, a 5-g weight is attached to the lower thick wire and the lower glass seal is then made [see Section 2(b) below], thus ensuring sufficient tautness in the wire. In order to minimize vibrational effects a small glass bead is sealed on to the inner wall of the lower end of the katharometer to which the lower thick platinum wire is anchored, as near as practicable to the thin wire, taking care not to block the tube to the flow of gas. The spiral in the thick platinum wire just below the glass bead ensures that the thin wire is mounted in a reasonably central position. A small hole in the base of the katharometer tube furnishes the outlet for the

nitrogen stream which then enters the gas-tight metal seal shown in *Figure 4*. This metal seal ensures robustness and rigidity to the delicate katharometer arms.

The two platinum wires from the inlets of the katharometer arms are made to form a common connection to the bridge by joining them through a screw connection to the top of the brass block. Any part of the column can thus be used for the common lead to the Wheatstone bridge. The platinum wires at the outlet ends of the katharometer arms are joined to an insulated terminal

Figure 3. Glass katharometer

A 49 s.w.g. *platinum wire* 4 in. *long*
B 22 s.w.g. *platinum leads*
C *Gas exit*
D 22 s.w.g. *platinum spiral*
E *Glass 'pip' sealed to wall*

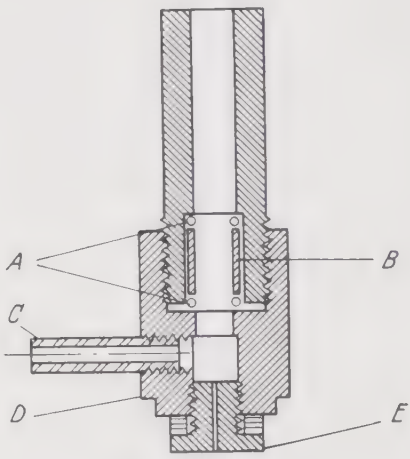

Figure 4. Metal seal

A *O-ring washers*
B *Brass ferrule*
C *Gas outlet*
D *Brass cap*
E *Tufnol plug*

block which is fixed to the base of the jacket of the block, enabling the copper leads to the bridge to be readily attached and ensuring that the differential temperature effects between the connections from the katharometer are minimized.

(*c*) *Assembly of column*—Celite 535 is used directly after vacuum drying at 140°C and is mixed with the appropriate liquid adsorbent. Glass tubes, 4 mm in diameter, are packed with the mixture after the manner described by James and Martin[2]. The open end of the tube through which nitrogen passes is inserted through a Tufnol plug at the top of the inner metal jacket (*Figure 1*) so that the top of the tube filling remains in the heated zone of the column. If the column is being run at a temperature below the boiling point of the sample under analysis, this top part of the tube is surrounded by a jacket which is heated electrically and the tube filling is extended into this zone so that the sample may be introduced at or above its boiling point.

The lower end of the column is drawn out to a taper and a piece of silicone rubber valve tubing placed over its end; this is inserted in the top of the katharometer arm thereby making a gas-tight seal. This tubing will withstand higher temperatures than ordinary rubber. A similar seal is used at the top of the column for the nitrogen supply.

The procedure which is generally favoured in this laboratory for the introduction of the sample is to add the sample from a 'capillary tipped' tube by touching the tube on to the top of the packing after interrupting the nitrogen stream[2]. *Figure 2* shows the method for assembling columns which are longer than 4 ft. The sections of the column are joined by short hairpin bends of stainless steel capillary tubing using small narrow-bore rubber stoppers to make the connections. 'Araldite 103' has been found very useful as a sealing material for these connections, ensuring that they are gas-tight. For work on materials which are corrosive towards stainless steel it is possible to use glass capillary connections.

2. Stability of katharometer

During the work carried out in this laboratory, Honeywell–Brown recorders have been employed. Both 1-mV and 2·5-mV (full scale deflection) recorders have been used. Ideally, when only pure nitrogen is emerging from the katharometer a vertical straight line would be traced on the recorder. In practice this line may suffer from two defects, namely those produced by movement of the pen of the recorder from side to side (wobble) and drift which is a continuous movement to one side.

When it is necessary to measure very small peak heights it is obviously desirable to produce a zero line which is as free from wobble and drift as possible and it follows that a great advantage is obtained under such conditions at very high sensitivities. It has been found that apart from the lower sensitivity of a 2·5-mV recorder compared with a 1-mV instrument it was easier to obtain a straight zero line because of its reduced susceptibility to random electrical pickup. Absolute currents of up to 100 mA, using a 6 V battery, have been employed in the katharometer wires.

(*a*) *Mechanical effects*—During the development of the apparatus described, mechanical effects which were responsible for instability of the zero (wobble) included vibration of the katharometer wire. This was overcome by constructing the instrument in the manner described above. In addition the whole apparatus was mounted on rubber blocks. It was of course necessary to ensure that the katharometer arms were firmly mounted at each end of the metal block (see *Figure 4*). The thick platinum wires leading to the metal block and junction terminal block were kept as short as possible.

(*b*) *Effect of tension on wire*—Whilst maintaining other conditions constant, the tension on the katharometer wire was varied between 1–10 g weight, the temperature of the column being given by boiling carbon tetrachloride. Least wobble of the zero of a 1-mV recorder was apparent when the tension on the wire was equivalent to 5 g weight. As the weight was decreased to 1 g, instability increased but not to a very marked degree; above 5 g instability again increased and was progressively more noticeable as the value was increased to 10 g.

(*c*) *Sensitivity: effect of current on katharometer wire*—It was found that for any individual katharometer there was a maximum value for the absolute current which could be applied to the wire, above which marked drift in the zero of the recorder trace resulted. This value was usually in the range 80–100 mA. The factors which govern this limiting value are under investigation. It seems possible that the point of drift might be reached at a lower

sensitivity with glass katharometers than with metal ones but comparative experiments need to be made. It is considered that there may be some rel-a tionship between the size of the air gap between the glass walls of the arms of the katharometer and the metal block, and the value of current before drift of the zero takes place.

It has been found that aging of the katharometer by normal use effects an improvement in the zero stability.

(*d*) *Boiling solvent: effect of reflux*—The procedure most usually employed for the return of reflux from the top of the column to the boiler was to allow the cooled liquid to flow through a pipe line directly into the boiler. This method was successfully used for carbon tetrachloride and water without causing marked movements of the zero line of the recorder. When, however, higher boiling solvents were used, including toluene (b. pt 110·6°C), ethyl cellosolve (b. pt 137°C), *cyclo*hexanone (b. pt 156·7°C) and ethyl hexanol (b. pt 185°C), marked erratic movements in the zero were encountered, even though precautions were taken to ensure that the substances were pure or of constant boiling point. This instability increased with increase in boiling point of the organic liquid. The difficulty was finally overcome by ensuring that the reflux returned directly down the column and at the same time was reduced to the minimum rate to ensure homogeneous temperature conditions in the column. A long air condenser was used for cooling the solvent and the heat input to the boiler was regulated to given the minimum reflux rate.

3. *Determination of* iso*propyl nitrate in 'heavy' oil*

(*a*) *Principle of method*—A particular problem for which vapour phase chromatography proved very useful was the determination of *iso*propyl nitrate which is added to 'heavy' oil as an improver. This represented a novel application of the technique in that it was an example of the determination of a volatile substance (b. pt 102°C) in a relatively non-volatile material.

The apparatus shown in *Figure 5* is an ancillary attachment which is connected to the inlet of a column 4 ft long containing dinonyl phthalate as the liquid adsorbent. The attachment has two tubes (length 10 cm, diameter 0·5 cm), namely a by-pass tube and a sample tube, both of which are about half filled with vacuum-dried Celite 535. By a suitable arrangement of taps the nitrogen stream can be made to pass through the by-pass tube or easily changed to the sample tube prior to passing through the column. The 'heavy' oil (containing *iso*propyl nitrate) is placed on the Celite in the sample tube which is heated under standard conditions when the *iso*propyl nitrate together with some light oil fractions, if present, are displaced on to the column. The nitrogen stream is then switched to the by-pass tube and the chromatographic separation of the *iso*propyl nitrate made in the usual way. Any light oil fraction displaced from the sample tube is not sufficient to interfere with the determination of the *iso*propyl nitrate.

(*b*) *Procedure*—It was considered that the use of an internal standard or marker would provide a suitable method for the measurement of the amount of *iso*propyl nitrate present in a sample of oil. Experiments with a number of liquids led to the choice of toluene, which under the conditions of operation was eluted approximately three minutes after the *iso*propyl nitrate.

A known concentration of toluene was added to the sample of heavy oil.

It is preferable to form a concentration of toluene which is near to that of the *iso*propyl nitrate.

The ancillary apparatus was heated to a temperature of about 150° C and the nitrogen passed through the column of dinonyl phthalate on Celite via the by-pass tube for a period of about ten minutes. The column was maintained at a temperature of 100° C using water in the boiler. The stream of nitrogen was diverted to the sample tube (previously conditioned as described for the

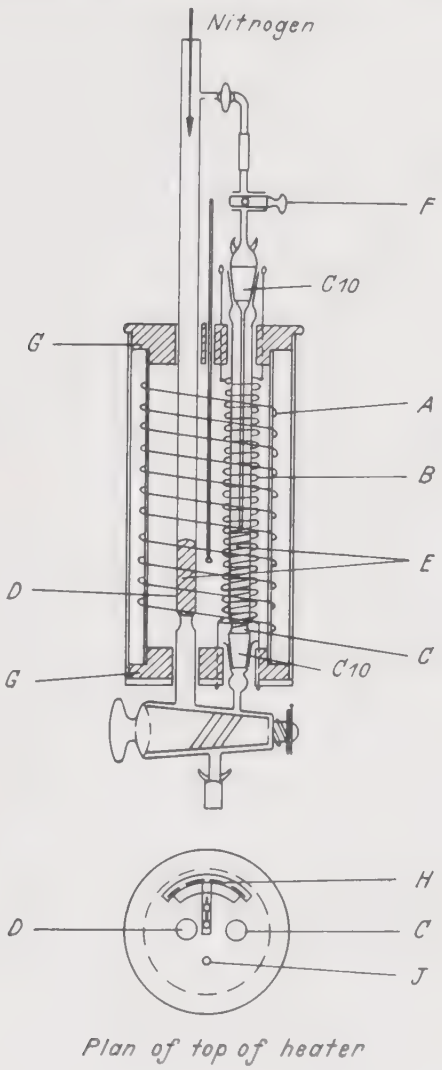

Figure 5. Auxiliary attachment for determination of isopropyl *nitrate in 'heavy' oil*

A 30 W *heater on glass former*
B Tube guiding and tension spring
C Sample tube in position
D By-pass tube
E Celite packing
F Special pipette
G Tufnol plug
H Variable vent for temperature adjustment
J Thermometer

by-pass tube) after inserting the ground glass socket attached to a tapered tube into which a suitable amount of the sample containing added toluene had been drawn. The tap on the inlet to the sample arm was closed and the tube and sample allowed to regain the temperature of the jacket, allowing a period of 45 seconds. After this time nitrogen was directed from the by-pass tube to the sample arm for a period of one minute in order to displace the *iso*propyl nitrate and toluene on to the column. It was then changed back again. These conditions gave a consistent and almost quantitative extraction of the

*iso*propyl nitrate and toluene with a minimum of background due to displacement of lighter boiling fractions from the 'heavy' oil.

(*c*) *Results*—The factor for peak height of toluene:peak height of *iso*propyl nitrate was obtained by analysing heavy oil containing known amounts of *iso*propyl nitrate and toluene. *Table I* shows the results obtained for the determination of the factor under the conditions given.

Table I. Determination of Toluene: iso*Propyl Nitrate Factor*

Column conditions
Composition Celite 535 + 30% dinonyl phthalate
4-mm diameter tube 4 ft long
Gas flow 18 ml per minute (atmospheric pressure)
Column pressure Inlet: 89 cm of mercury
Outlet: 21 cm of mercury
Current on katharometer wires 90 mA
Sensitivity for *iso*propyl nitrate: 1·0 mV per 1 mg
Retention times *iso*Propyl nitrate: 6 min
Toluene: 9 min
Temperature of column 100°C
Temperature of ancillary heater 150°C

Toluene added to oil % by vol.	iso*Propyl nitrate added to oil* % by vol.	*Peak height toluene* / *Peak height* iso*propyl nitrate*
0·25	0·25	0·79
0·50	0·50	0·72
1·0	1·0	0·78
1·5	1·5	0·81
2·0	2·0	0·79
3·0	3·0	0·80
4·0	4·0	0·81
10·0	10·0	0·82
20·0	20·0	0·83

Mean factor 0·79

Table II. Determination of iso*Propyl Nitrate in Mixtures with 'Heavy' Oil*

iso*Propyl nitrate present* % by vol.	*Toluene added* % by vol.	iso*Propyl nitrate found* % by vol.
0·25	1·0	0·24
0·25		0·27
0·50		0·49
0·50		0·50
2·0		1·99
3·13		3·18
3·13		3·06
3·13		3·01

Table II shows the amounts of *iso*propyl nitrate found when added in amounts ranging from 0·25–3 per cent. The amount of toluene added was

kept constant at a value of 1 per cent. The mean factor obtained from *Table I* was used to calculate the amounts of *iso*propyl nitrate. Consideration of the results obtained indicates an accuracy which is usually better than ±5 per cent.

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DISCUSSION

D. Brennan: There is a considerable amount of evidence, obtained from both general experience and specific experiment, indicating that the shorter the time taken to get the sample on to the column the better the resolution obtained in the subsequent analysis. The limit is instantaneous evaporation of the sample and this may

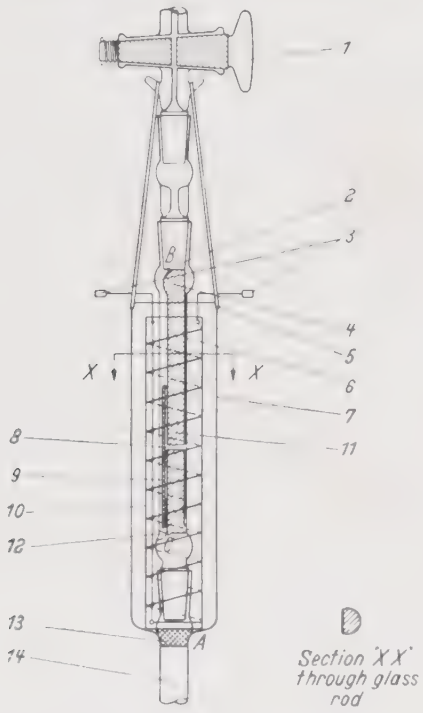

Figure 6. The controlled-heat capillary tube

1, Spring-loaded stopcock (controlling gas flow). 2, Gas inlet. 3, Lead to electric supply. 4, Cone fused into glass rod. 5, Rubber bands connected to heating jacket. 6, Ancillary tube. 7, Glass jacket, sealed to column. 8, Minimum clearance. 9, Capillary tube. 10, Heating coil wound on glass former (25 s.w.g. Nichrome wire). 11, Glass rod, fused into ancillary tube. 12, Gas outlet. 13, Glass yarn, on top of column packing. 14, Column

be approximated to by explosive evaporation. The sample is sealed into a thin-walled capillary tube and the charge is delivered to the column by heating (by means of an external electrical heater) until the tube explodes; the small capillary tube is contained in a 3 mm bore thick-walled capillary plugged on at the head of the column. With a suitably (but not excessively) thin-walled capillary the temperature of explosion with e.g. diethyl ether is about 100 C. The method seems to possess all the advantages of that described by Mr Williams, namely, small chamber volume, accurately known sample size and ease of applicability at high

column inlet pressures but in addition it has the feature of extremely rapid evaporation of the sample.

A. F. WILLIAMS: We considered Dr Brennan's method was not an improvement for it was not very precise and he has no control over the transfer of the sample to the column. Moreover, it might be difficult to select a glass tube which was sufficiently thin.

In our apparatus shown in *Figure 6*, we have complete control over the conditions of transfer; the capillary tube can be heated to any desired temperature of injection and the tube broken after any chosen time of heating. No special selection of wall thickness of capillary tube is necessary.

We suggest that the apparatus we have described is specially suitable for the study of reaction kinetics on very small amounts of material.

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THE ANALYSIS AND CONTROL OF REFINERY GAS STREAMS USING THE CHROMATOGRAPHIC TECHNIQUE (JANAK METHOD)

C. Rouit
Société Française des Pétroles BP

This paper aims at demonstrating how the almost diagrammatic application of adsorption or partition vapour phase chromatography principles provides a refinery laboratory with a simple and accurate method of gas analysis for routine control. It is carried out by means of the Janák technique in which carbon dioxide is used as carrier gas and direct measurement made of eluted components after caustic potash absorption of the carbon dioxide.

The apparatus employed is essentially laboratory standard equipment and it is constructed in such a way as to require very simplified handling. The chromatograph columns are of three main types: partition columns of dimethylformamide on Fosalsil, adsorption columns of either activated alumina or carbon. They are operated only at room temperature. Reference chromatograms have been established to allow the most suitable type of column for a given type of gas sample to be chosen.

Illustration of the method is given by its application to routine analysis of Platformer gas samples.

In a comparatively short period of time the method of gas and vapour analysis involving the elution technique in adsorption or partition chromatography has become widely used on account of its outstanding qualities of simplicity, rapidity and accuracy. It is unnecessary to go over again the historical development of the method, the matter having already been repeatedly dealt with[1,2].

The various forms of apparatus employed are particularly characterized by the variety of detecting devices. Whereas a suitable chromatograph column is determined by the nature of the mixtures to be analysed, the choice of detecting method is more a question of ease of construction. James and Martin's gas density balance[3] and the surface potential detector of Phillips *et al.*[4] can hardly be constructed by any laboratory lacking workshop facilities; they are somewhat delicate to maintain and operate. Phillips's[5] or Ray's[6] thermal conductivity detectors are easier to construct; but Janák's[7] gas volume detector is, in contrast, appropriate to everyone, provided only gas analysis is concerned.

It will be shown that the most unpretentious of detectors fitted to the simplest of chromatograph instruments is able to do valuable work in an

important analytical field, that of routine analysis of refinery gaseous hydrocarbons.

The various problems created by gas production during crude processing or during cracking and reforming treatment of certain petroleum fractions are numerous, e.g. industrial plant regulation, product output balance, checking of commercial liquefied gases (butane and propane). Equally numerous are the various means of analysing these gases: distillation (Podbielniak), i.r.- and mass-spectrometry are the most outstanding. Among these the most commonly used is undoubtedly the Podbielniak type distillation, but these analyses are notoriously long and the apparatus demands skilled handling. The refiner who does not possess a mass spectrometer is in frequent need of a short and accurate method allowing controls to be multiplied without the need of highly trained personnel, which are sometimes hard to secure at sites remote from large towns.

The Janák type of chromatographic apparatus adequately meets these requirements, either alone or as a complement to existing techniques.

This description will consequently deal with an extremely simple apparatus, but experience has proved its excellent efficiency in meeting the needs of routine analysis.

Janák Technique of Analysis

The arrangement of the apparatus is given in block-diagram form in *Figure 1*. The carrier gas (carbon dioxide), is delivered from *AA'*, flow control taking

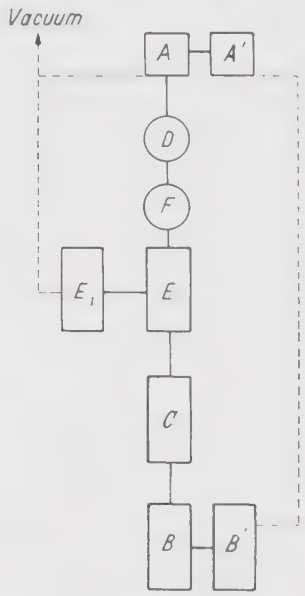

Figure 1. Arrangement of apparatus (schematic)

place in *F*, runs through *E*, EE_1 being the sample inlet system, proceeds through the chromatograph column *C* and emerges to be absorbed in a concentrated potash bubbler. A gas micro burette is fitted over the bubbler to collect unabsorbed gaseous components of samples to be analysed and allows measurement readings under atmospheric pressure (*BB'*).

The apparatus was built to allow column operation *at room temperature*: as a rule the C_3–C_5 hydrocarbon gases may be eluted easily from partition columns at this temperature, whereas Janák, making use of solid-adsorbent

columns only, was compelled to heat these columns to analyse the same hydrocarbons. The types of column were selected in order to reduce their number and the apparatus was constructed such that only standard laboratory materials were used and operation would be very simple.

The apparatus

Powdered solid carbon dioxide is stored inside trap A_1 (see *Figure 2*). Preliminary powdering of the solid carbon dioxide and storing in a Dewar

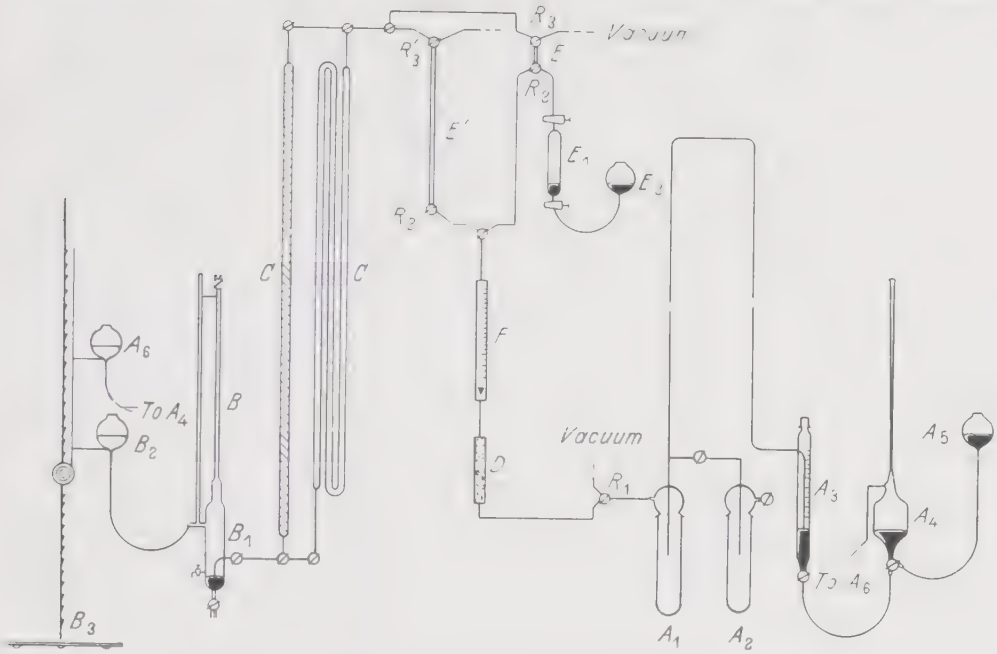

Figure 2. Gas chromatography apparatus (Janák method)

vessel eliminates most of the permanent gases (air) included in it. A_1 receives sufficient charge to last one day and is then evacuated to 0·1 mm of mercury, while being immersed in liquid nitrogen. This operation is repeated if necessary. Should the solid carbon dioxide be of poor quality, it may be distilled from A_2 to A_1, but this takes some time.

After complete elimination of permanent gas, the initial carbon dioxide pressure is fixed by immersion of A_1 into a mixture of acetone and solid carbon dioxide between —20 and —40 C, and by adjustment of the mercury level in trap A_3, from which excess carbon dioxide escapes continuously. Then the carbon dioxide stream is led through the adsorbing column D filled with calcium chloride and coarse-grained indicator silica gel followed by a rotameter F acting as flow indicator. The gas next proceeds through either E or E' standard volumes before reaching either column C or C'; on emerging it is collected in bubbler B_1 for absorption by 45–50 per cent potash.

Once carbon dioxide flow has been established and air duly flushed from the apparatus, the potash level in the micro burette is adjusted and noted, the flow of carbon dioxide is stopped by closing stopcocks R_2 (or R'_2) and R_3 (or R'_3). The assay sample is transferred into the corresponding standard

volume E (or E') from the gas bulb E_1 in which the total sample is kept. To do this E (or E') is first evacuated to 0·1 mm of mercury up to stopcock above E_1 and gas is then admitted under atmospheric pressure by action of the mercury bulb E_2. The volume of the assay sample is therefore determined initially by the standard volume: a 1·5 ml standard volume is used for routine analysis (small standard volume E); for determination of minute amounts of component, a 10-15 ml standard volume is necessary (large standard volume E').

Where checking is frequent the taking of assay samples may be simplified: the bulk sample can be taken in a rubber bladder which is attached to the usual bulb E_1. This rapid procedure is valid only where the analysis is carried out within half an hour following sample taking, as experience has proved that after this time, gas diffusion through the bladder walls greatly alters the proportions of the components.

Gas having been admitted into E (or E') the carrier gas stream is re-established by opening stopcocks R_3 (or R'_3) and R_2 (or R'_2). This action marks the *zero time* for the analysis. Components of the mixture are eluted through the chosen column and after a certain delay the first gas appears in the micro burette. A curve (chromatogram) is plotted showing the increase of the collected volume against time. Readings on the micro burette are taken under atmospheric pressure, the movement of potash bulb B_2 (mounted on a rack) allowing adjustment of levels in the micro burette and the reference tube which has the same diameter as the graduated tube.

During the course of analysis the potash level in the micro burette is lowered and the pressure at the outlet of the column decreases. In order to maintain fairly even flow through the column, the inlet pressure must be adjusted by an equivalent quantity. This adjustment is easily made by means of the compensation system A_4-A_6, which affects the level of mercury in valve A_3: the level in A_4 varies in parallel with the level in micro burette B, following the movements of bulb A_6, which are identical to those of bulb B_2. The liquid in A_4-A_6 is a saturated solution of potassium carbonate, density 1·6. Flow adjustment is very satisfactory under such conditions, and it allows regular chromatograms to be obtained.

The micro burette volume is 4 ml, with 0·01 ml graduations; the inside diameter should not be under 4 mm to avoid formation of gas locks during elution.

When using the standard volume above, 4 ml (E'), it would logically be better to use a gas burette fitted with a graduated receiver of equivalent volume. This solution is not excluded and it is obviously possible to rearrange a second special micro burette, into which the carrier gas flow can be diverted at will. But, in general, the 4 ml burette will be sufficient: a preliminary analysis on a small volume is necessary for checking the retention time of components existing in the form of minute amounts, and the following analysis is carried out with a larger volume, successive components being eliminated from the burette after readings by quickly restoring the previous potash level. Analysis of minute amounts is thus obtained with greater accuracy, requiring a little more skilled handling from the operator.

Two chromatograph columns are illustrated in *Figure 2*. It will be shown later that the analysis of mixtures consisting of permanent gases (hydrogen,

air) and saturated hydrocarbons up to the pentanes requires, for completion, the use of two separate columns and it is therefore convenient to have them fitted permanently. Replacement of a column is obviously a very simple and rapid operation, but flushing out the air admitted during the operation must follow, which results in a loss of time.

The chief difficulties encountered during analysis result from possible leaks in the sample transfer system: in particular the soundness of stopcocks enclosing standard volumes is of utmost importance. Lubrication of stopcocks is a real problem on that account and it is imperative that good quality vacuum grease which does not dissolve hydrocarbons is used. Silicone grease is mostly employed but has a tendency towards absorbing, particularly, unsaturated hydrocarbons. Phosphoric acid is an excellent lubricant but affords poor resistance to vacuum.

The chromatogram obtained with the technique described is composed of successive steps. Compounds are qualitatively characterized according to 'retention time', which means the time spent between introduction of the compound into the column and production of the corresponding step (measured at the inflection point); the preliminary marking of retention times for individual components can be obtained, if needed, by the use of pure hydrocarbons or mixtures of definite composition. Quantitative measurement is obtained from the measured height of the chromatographic step.

Chromatograph columns

Two categories of columns are used: active adsorbent columns and partition columns.

Adsorbents employed—These are: (*1*) active carbon 'Acticarbon NCP-50', Tyler mesh 40–50 (produced by Carbonisation et Charbon Actif, CECA, Paris); (*2*) Davison silica gel, 28–100 mesh (obtained by the sifting of grade 12 Davison gel as produced by Davison Chem. Corpn, Baltimore, U.S.A.; (*3*) activated alumina, 'Gammagel–Electro', 40–50 mesh (as produced by Electrochimie–Ugine).

After careful sifting, these products, alumina excepted, are dried in an oven for a minimum of 3 hours at 130 C. The activity of alumina is strongly dependent on its water content so that it must be treated for a longer time: for the indicated variety of alumina, the treatment is for at least 16 hours at 160 C. Active adsorbent columns are 800 and 1800 mm in length and of 6 mm inside diameter.

Partition column packings—These consist of a solid support (inert porous material) impregnated with a solvent of hydrocarbons (immobile liquid phase).

The solid support is Fosalsil, a refractory material of diatomaceous earth (as produced by Moler Products, Colchester). A 50–100 mesh fraction freed from dust by water and dried to constant weight at 110 120 C is employed.

Stationary phase liquids, chosen for their selectivity, are polar compounds: (*a*) dimethylformamide, principally; (*b*) dibutyl and dioctyl phthalate; and (*c*) nitrobenzene.

Fosalsil is impregnated with these liquids to 50 per cent by weight. Columns are 1800 mm in length (and, rarely, 3000 mm) and of 7 mm inside diameter.

Selection of the type of column to use depends on the nature of mixture to

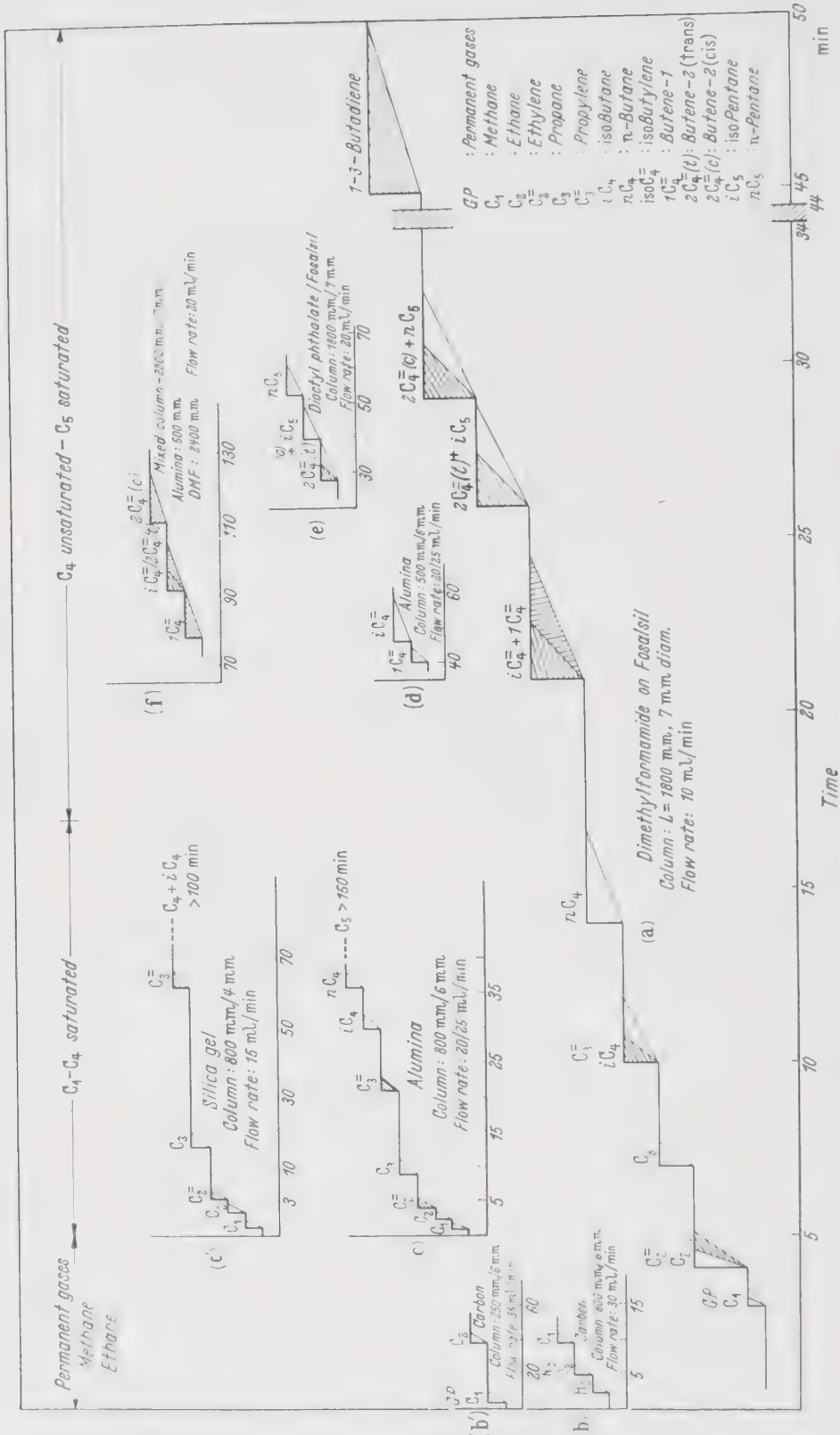

Figure 3. Reference chromatograms

be analysed and the scheme is as follows: (*i*) active carbon columns for permanent gases—methane (ethane); (*ii*) silica columns for C_2 C_3 hydrocarbons, saturated or unsaturated; (*iii*) alumina columns for C_1–C_4, saturated or unsaturated; and (*iv*) dimethylformamide on Fosalsil for C_1–C_5 (saturated), C_4 (saturated and unsaturated).

The analysis of complex mixtures may require repeated operation with two or more distinct columns or even composite columns.

We have therefore made out a *summarizing diagram* as a guide to chromatographic analysis (*Figure 3*). It is based on a reference chromatogram [*Figure 3*(a)] grouping gases of interest from the way they are separated by the most used partition column (dimethylformamide on Fosalsil) considering their elution times at known flow rates. Mixed steps are next broken down so as to lead to complete resolution of all individual constituents [*Figures 3*(b)–(f)].

Interpretation is very simple and allows a rapid selection of the column which should be used to analyse refinery gases of constant qualitative composition.

The number of mixed steps evident in *Figure 3*(a) may suggest that the *partition column with dimethylformamide* is of limited use. Its value will, however, be realized if note is taken that it allows, in particular, a very rapid analysis of every saturated hydrocarbon gas mixture (e.g. direct refinery gas, Platformer gas as illustrated below), and of every C_4 hydrocarbon gas mixture, saturated and unsaturated, including a very distinct separation of *cis*- and *trans*-butene-2, and of butadiene, the separation of butene-1/*iso*butene alone being at fault (e.g. in the particular analysis of a C_4 cut from thermal reformer or vapour phase cracker, *Figure 5*).

Active alumina adsorption columns are considered to be next in importance to the dimethylformamide columns; the reason for this preference is evident from *Figure 3*(c), which indicates the real efficiency in rapid separation of C_1–C_4 hydrocarbons, including ethylene and propylene (viz. analysis of fuel gas, gaseous fractions with predominant C_2 or C_3 hydrocarbons). Alumina columns must also be credited with the separation of butene-1/*iso*butene in corresponding binary mixtures, this possibility being of little use, however, owing to the butene-2 isomers interfering in a mixture of the four compounds (*Figure 6*).

Finally *active carbon adsorption columns* are indispensable when the samples contain permanent gases, e.g. hydrogen, air or methane, in particular. Should these three be the only components, detailed analysis results from complete elution; should other hydrocarbons be present, elution is not conducted beyond methane (or ethane if special use is made of a two-part column mentioned in connection with Platformer gas control described later) and this incomplete analysis only brings out the proportions of these three components. In this second case, the same column may be used only for some four or five successive runs, before renewal of the adsorbent becomes necessary. This is a disadvantage inherent in analyses by displacement chromatography (*Figure 7*).

Introduction of partial analysis brings us to a field where chromatographic analysis can reach a greater complexity, due to the successive use of several distinct columns for complementary resolutions. Apart from analyses

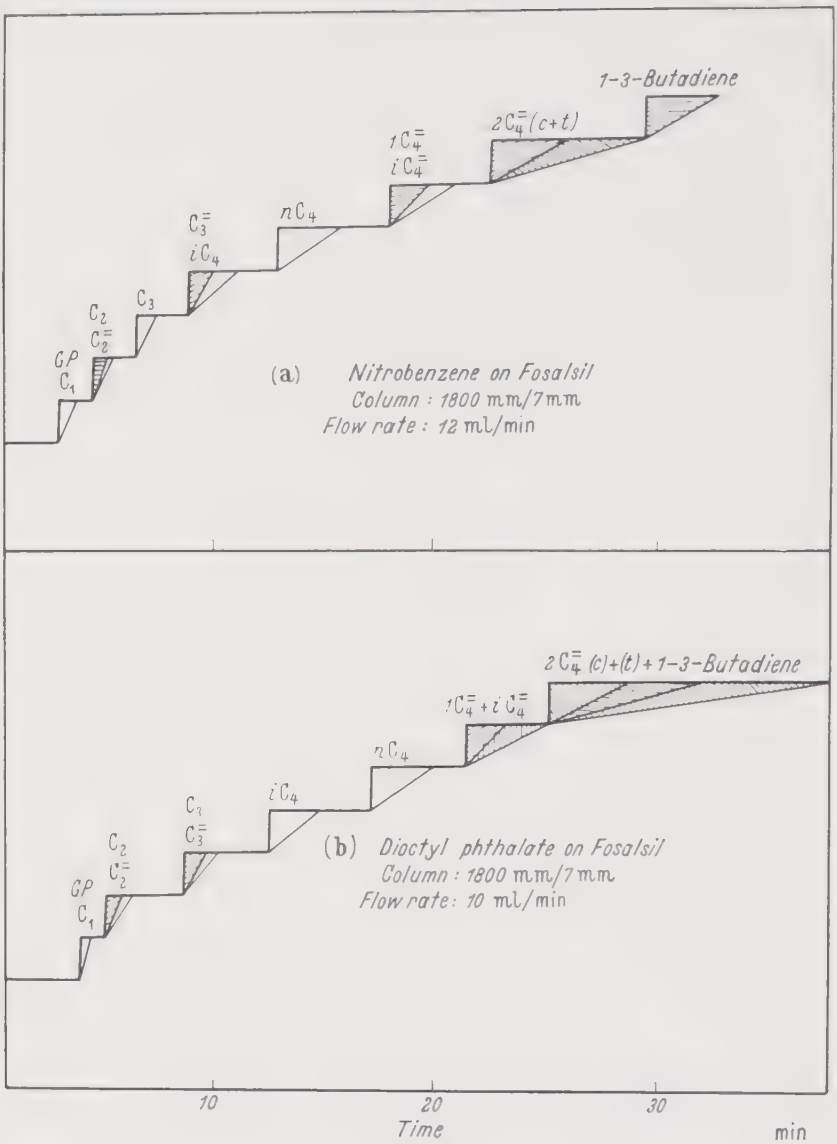

Figure 4. Further reference chromatograms

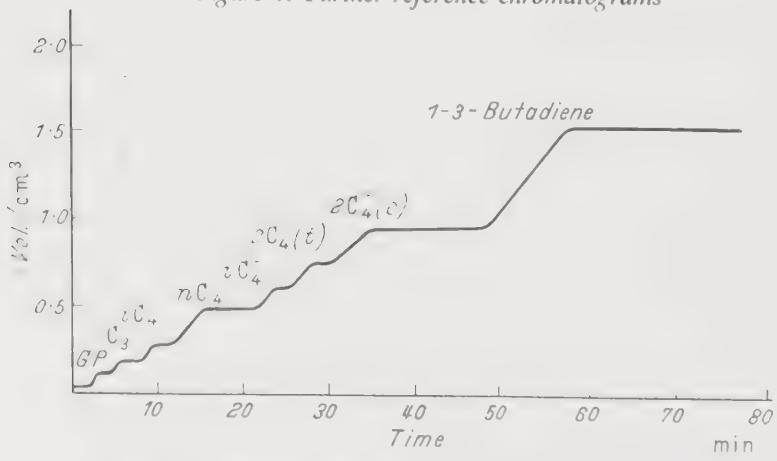

Figure 5. Chromatogram using Fosalsil/dimethylformamide. Column: 1800 mm/7 mm. *Flow rate* (CO_2)*:* 10 c.c./min

required for control of a Platformer plant, which by chance remain very simple, the technique is mostly used for special cases which are seldom met in routine control. That which is considered the most complex is illustrated.

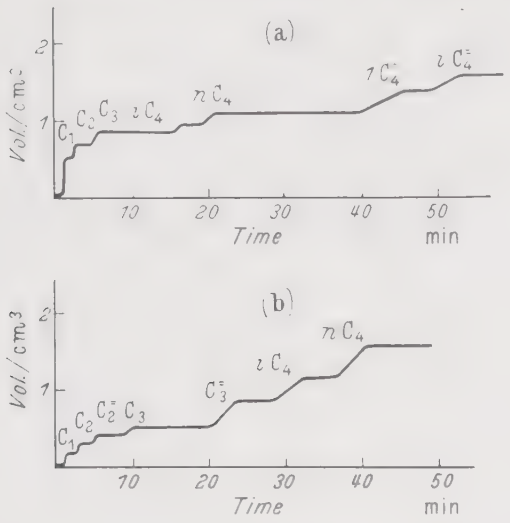

Figure 6. Chromatograms on alumina:
(a) *column* 500 mm/6 mm. *Flow rate* 30 c.c./min;
(b) *column* 800 mm/6 mm. *Flow rate* 20 c.c./min

Take, for instance, a mixture of the eight components: *iso*butane, *n*-butane, the four butenes, *iso*pentane and *n*-pentane; total analysis can be completed with the aid of two columns:

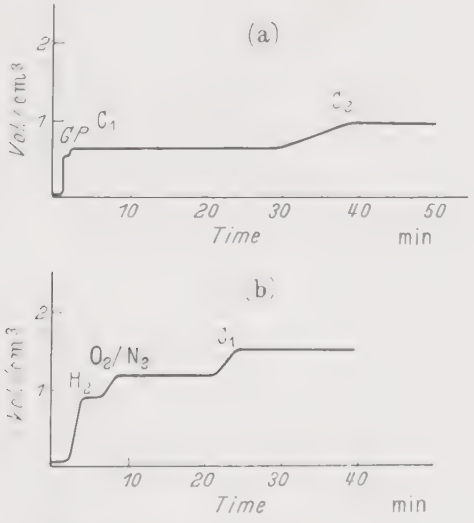

Figure 7. Chromatograms on carbon:
(a) *column* 250 mm/6 mm. *Flow rate:* 35 c.c./min;
(b) *column* 1800 mm/6 mm. *Flow rate:* 20 c.c./min

(*l*) Dioctyl phthalate partition column which will yield: *iso*butane *n*-butane/butene-1 + *iso*butene/*cis*- + *trans*-butene-2/*iso*pentane/*n*-pentane [*Figure 3*(e)].

(2) Mixed column with two sections mounted in series, one 500 mm long of alumina, one 2400 mm long with dimethylformamide which will yield: *iso*butane/*n*-butane/butene-1/*iso*butene + *trans*-butene-2/*cis*-butene-2 + *iso*pentane/*n*-pentane [*Figure 3*(f)].

Binary systems are easily determined by combination of both analyses. Results can then be checked by means of a third analysis with a dimethylformamide column, which will yield in a short time: *iso*butane/*n*-butane/butene-1 + *iso*butene/*trans*-butene-2 + *iso*pentane/*cis*-butene-2 + *n*-pentane.

This type of analysis is evidently fairly slow, the more so on account of the delay imparted by elution on the mixed alumina–dimethylformamide column. It is plainly understood that only the minimum and most simple apparatus is considered here: it will easily be appreciated that, without undue expense or complication, a more complete apparatus could be produced, allowing for two or more simultaneous analyses, apart from the routine control apparatus.

Separations obtained through the above means are, on the whole, of fair quality dependent on the distinctness of the levels between two successive elution steps. In that respect, mention should be made of the influence shown by concentration on the spreading of elution steps, the direct consequence being a reduction in the level length: when two compounds A and B are eluted one after the other, the level between the two steps is always more distinct when the concentration of A is less than that of B. This evidently poses a problem. The only difficulties ever experienced in this respect concern analysis of C_4 hydrocarbons, particularly those having fairly large retention times on solid adsorbents (*iso*butane and butane on one side, butenes on the other), and the analysis of minute amounts of components in the presence of a large concentration of a major component.

The accuracy of analysis, deduced from analysis of synthetic mixtures, is very satisfactory: it is better than 1 per cent absolute in 80 per cent of cases, and always better than 2 per cent absolute. Reproducibility is similar. The most important errors occur in connection with samples involving large amounts of pentanes, which is easily explained. It is likely that longer practical application of the method will compel the opinion that the accuracy is even better than predicted.

Some types of columns listed above have not yet been described.

Adsorption columns of silica gel may be used for C_1–C_3 hydrocarbons [*Figure 3*(c′)], likewise alumina columns, but retention times are longer; moistening silica gel is an artificial way of shortening retention times, but obtaining homogeneous lots of silica gel is difficult.

Partition columns of dioctyl or dibutyl phthalate [employed for partial resolution of butenes, *Figure 3*(e)] or of nitrobenzene will allow some resolutions similar to those with dimethylformamide. Incidentally, reference chromatograms for these columns are shown in *Figure 4*.

To conclude and as an illustration of routine application we shall describe the use of the Janak method during control of Platformer gases. Two types of mixtures are chiefly of interest for this process:

(*a*) Recycle gases, including 70–80 per cent (vol.) hydrogen, 5–15 per cent methane and smaller or minute quantities of saturated hydrocarbons up to C_5.

(*b*) Stabilizer overhead gases, the raw product for commercial propane and

butane, including small quantities of hydrogen besides C_1 C_4 saturated hydrocarbons in various proportions, and minute amounts of C_5.

Total analysis of these two gases can be entirely carried out using two different columns, the small or large standard volume being used as needs be, allowing various combinations as follows:

(*1*) Partition column of dimethylformamide and large standard volume: this will give $(H_2 + C_1 + C_2)$ and C_3–C_5 separately.

(*2*) Same column and small standard volume: with restricted flow (10 c.c./min) of carrier gas, will give $(H_2 + C_1)/C_2$–C_5 separately, provided minute amounts are not concerned.

The active carbon adsorption column employed next is of special construction (*Figure 8*).

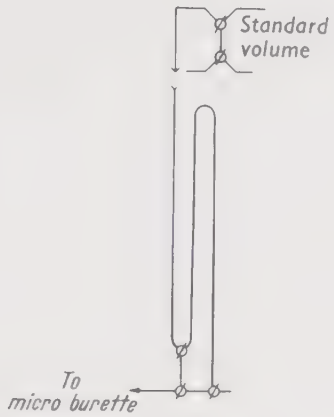

Figure 8. Arrangement of two sections column

This column is built with first a 150 mm/6 mm section ending with a 3-way stopcock; the first outlet is directly connected to the gas burette while the second leads to a further section 1500 mm/6 mm connected to the gas burette. Adjustment of the stopcock permits use of the total length of both sections (1650 mm) or of the single first section or of both, one after the other, as desired. Thus the column facilitates the following partial analysis:

(*3*) Complete column, small standard volume: rapid analysis of H_2/CH_4.

(*4*) First section of column, large standard volume: (total $H_2 + CH_4)/C_2H_6$, common technique employed when small quantities of C_2H_6 are present.

(*5*) Lastly, successive use first of the total length then of the short column section with the large standard volume will allow in one simple operation both (*3*) and (*4*) analyses provided the large gas burette with a volume equivalent to the large standard volume is used. Procedure is as follows: after introduction of sample, the whole of the column is in circuit: permanent gases and methane reach the second section in which their separation is completed and individual measurement is taken, C_2H_6 remaining all the while in the first section; after elution of CH_4, the first section is directly connected to the gas burette. The flow rate is automatically increased and C_2H_6 is collected within a relatively short time. From these results the analysis of H_2/(air)/CH_4/C_2H_6 may be obtained.

The above description points out the advantages and versatility of an apparatus fitted with two columns. Hydrocarbons not eluted from a carbon

adsorption column (above C_3) are held back in a short section, which is easily renewed. For the analyses of Platformer gases a wide choice is available from the variations possible.

For recycle gases, the most important information required is the hydrogen content: operation is conducted as in (*3*). This analysis recurs most frequently (*Figure 7*). Should detailed information as to hydrocarbon contents be desired, the analysis takes place successively as in (*1*) and (*5*), if the large volume gas burette is available, or as in (*1*)-(*3*)-(*4*) if not available: this type of analysis is the least frequent.

For stabilizer overhead gases, operation as in (*2*) and (*3*) has proved satisfactory. This analysis is also very common: it is illustrated in *Figure 9*.

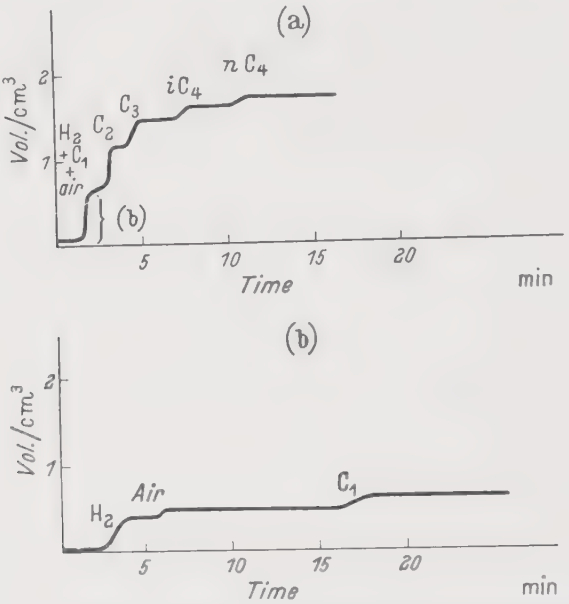

Figure 9. Analysis of stabilizer gas (Platforming)

in which (a) is a chromatogram plotted according to (*2*), and (b) the partial chromatogram corresponding to the resolution of the first step in *9*(a) according to (*3*).

Conclusion

We have endeavoured to demonstrate what help could be expected from the chromatographic method in routine refinery gas analysis. Rational use of three main types of columns, alumina or active carbon adsorption columns and dimethylformamide partition columns, allows easy execution of essential routine analysis with adequate rapidity and accuracy for normal control.

Based on the very simple apparatus described, additions can obviously be made which without excessive complication would allow more complex problems to be investigated, making the Janak technique valuable for research work.

We wish to thank the Executive Board of the Refining Department of the 'Société Française des Petroles BP' who kindly authorized this paper and also our friends of The British Petroleum Company Limited, who drew our attention to the chromatographic method of gas analysis.

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DISCUSSION

F. van der Craats: Our experience with the Janák method is also very favourable. It can, for instance, completely replace the combustion technique for determining hydrogen and methane. For plant control the apparatus has to be as simple as possible. A sufficiently constant current of carbon dioxide can be obtained by placing a needle valve just before the sample inlet system. This renders superfluous the manipulation with levelling bulbs during the analysis. The readings of the nitrometer are corrected for pressure differences with the aid of a simple graph. Corrections for barometric pressure and temperature are negligibly small.

R. Sigwalt: I appreciate very much the simple and elegant method that Mr Rouit described. I have only one question to ask: what are the lowest amounts of a component for which the analysis with this method will give significant results?

C. Rouit: I should like to refer to Mr van der Craats's question on the compensation system. This is used mainly when analysing mixtures with a high concentration of hydrogen as it avoids the formation of gas locks in the burette when the hydrogen comes through very quickly.

With regard to Mr Sigwalt's question, Janák's technique allows detection of a component comprising 0·3 vol.% of the original mixture, when using the small standard volume of 1·5 ml. We can say that a good operator can 'perceive' smaller quantities by observation of the size of the bubbles in the burette.

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PRACTICAL NOTES ON GAS–LIQUID CHROMATOGRAPHY AS APPLIED TO THE ESTIMATION OF VOLATILE FATTY ACIDS

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The modifications to the automatic titration apparatus of James and Martin (1952) include a polythene gland incorporating a mercury seal for the recording burette, an automatic switch-off device for the apparatus, and a photoelectric unit which provides stable and full control for continuous operation.

A new procedure has been devised for converting soap solutions to acids and transferring them quantitatively to chromatograph columns without removing the columns from the vapour jacket. For this purpose a modified chromatograph column and a glass reaction vessel for converting soaps to acids have been designed.

The factors affecting the effective life of chromatograph columns have been discussed and attention has been drawn to the possible use of *o*-tricresyl phosphate as an alternative liquid phase for the analysis of the lower volatile fatty acids.

The gas–liquid chromatographic procedure of James and Martin[1,2] provides the chemist with an ingenious technique for the analysis of titratable volatile organic compounds. This method has since been extended to cover a wide range of neutral organic compounds[3–7] and gases[8] through the development of other recording devices[3,5,6,8,9] capable of detecting and measuring small changes in the composition of the mobile phase. In this laboratory the automatic titration apparatus of James and Martin[1] has been used for the estimation of volatile fatty acids occurring in animal depot fats[10,11]. During the course of this work the technique has been improved by modifying the apparatus and methods for preparing samples for analysis. A detailed study has also been made of the factors affecting the useful life of chromatograph columns[12].

Modifications to Apparatus

Gland on recording burette

On their original apparatus[1] James and Martin had a 'Telcothene' gland on the recording burette at one end, through which passed a 0·125-inch diameter stainless steel rod. The rod, of necessity, had to be a tight fit in order to prevent leakage of alkali back through the gland. Any slight variations in the diameter of the rod should theoretically have been compensated by the inherent elasticity of the plastic. In our experience this gland was not

satisfactory and had a tendency to crack and leak, so a polythene gland incorporating a mercury seal was designed (see *Figure 1*). Parts *A* and *B* are threaded so that they can be screwed together. To assemble, the chromium plated precision ground steel rod *D* is introduced into sleeve *Bb* until it projects into well *C*. Well *C* is then filled with mercury, and *A* is screwed into *B*, displacing mercury through sleeve *Aa*. The rod is then pushed through *Aa* trapping a pool of mercury in well *C* which prevents alkali leaking back through the gland. Although a scale drawing is given in *Figure 1*, the dimensions of the gland are not critical. The rod should slide easily through the

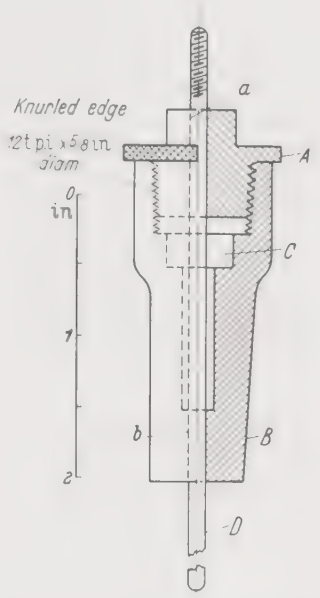

Figure 1. Plan view of polythene gland incorporating a mercury seal; half in cross section

A, Gland cap; B, gland tapered to fit B24 'Quickfit' socket. A and B can be screwed together; C, well for mercury; D, burette plunger (0·125-inch diameter chromium plated precision ground steel rod) threaded at one end for connecting to carriage; Aa and Bb, sleeve (0·125 inch diameter) for burette plunger

gland which is readily fabricated, robust, and does not have to be machined as accurately as the original gland. The latter, however, may function satisfactorily if a precision ground rod is used instead of one of stainless steel.

Photoelectric control unit

Since the apparatus has been used principally for estimating volatile acids up to decanoic acid, and is in continuous operation for periods of 100 hours or more, it is essential that the photoelectric control unit provides full and stable control. The original amplifier[1] was sensitive to power fluctuations and had a tendency periodically to lose control. A new unit was designed (see *Figure 2*) which incorporates a.c. regulation on account of the high sensitivity of the circuit. The saturable transformer feeds T_1 and T_2 while T_3 and T_4 are fed directly from the mains. Thus all the heaters, the 12V lamp and the 5V4 h.t. supply are regulated while the phase-shift circuit transformer T_4 and the motor supply transformer T_3 are not. Neither of these two latter circuits is mains sensitive to any great degree. A suitable Thyrite non-linear resistor is connected from the anode to the cathode of the GT1C to reduce the high current during motor starting. The lamp and photocell housings have

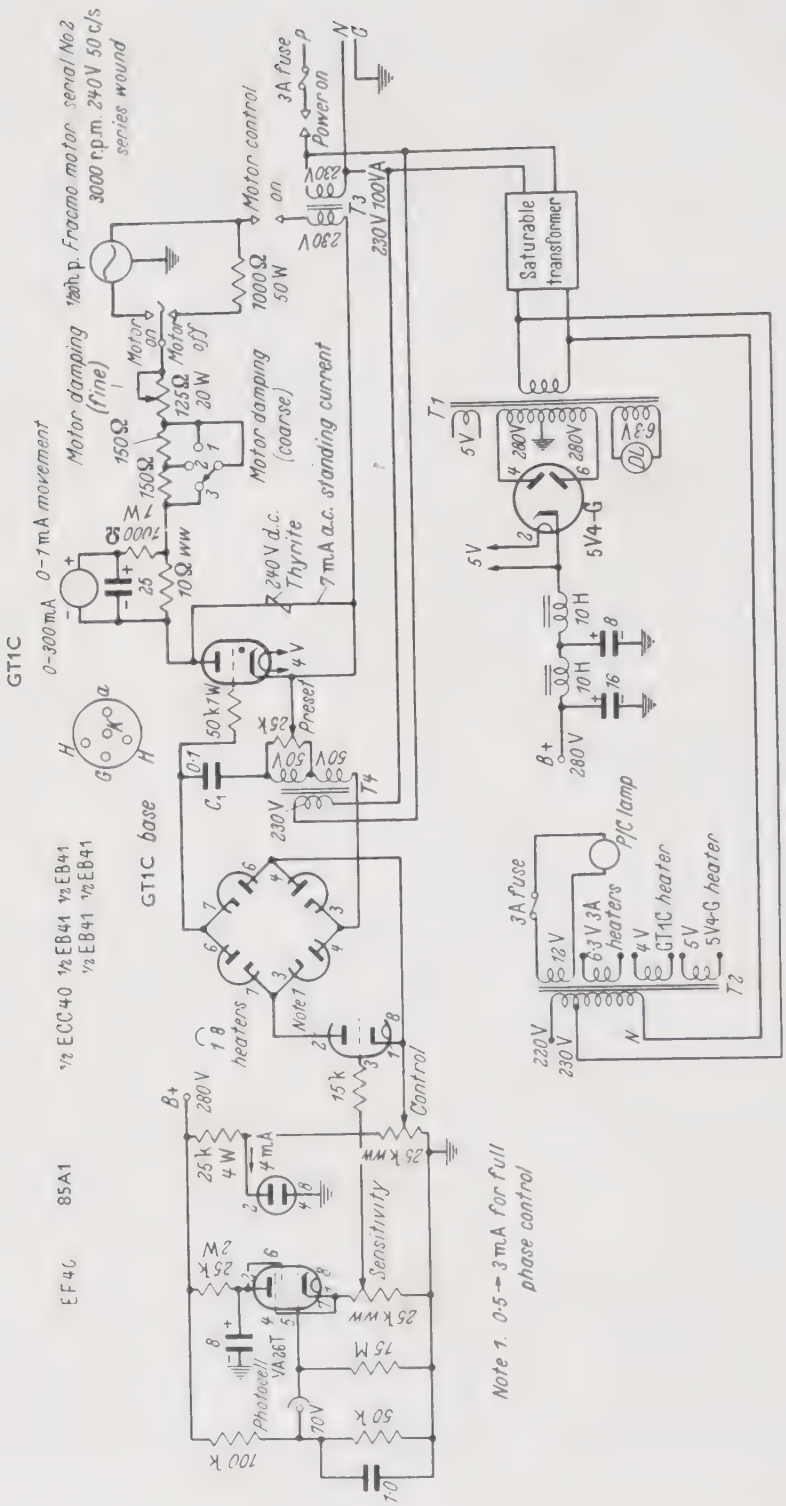

Figure 2. Circuit diagram of photoelectric control unit for volatile fatty acid estimation

been constructed as a unit (see *Figure 3*) which prevents extraneous light reaching the photocell and eliminates the necessity of regulating adjustable shutters, as on the original photocell housing[1], to suit the intensity of light in the room from day to day. It is equipped with a fitting suitable for support by a standard retort stand. The section of the titration cell in front of the light source and photocell is completely enclosed, and thus ensures uniform conditions for titration. When in position the unit need not be removed from the titration cell to renew the lamp, and photocell replacements can be made

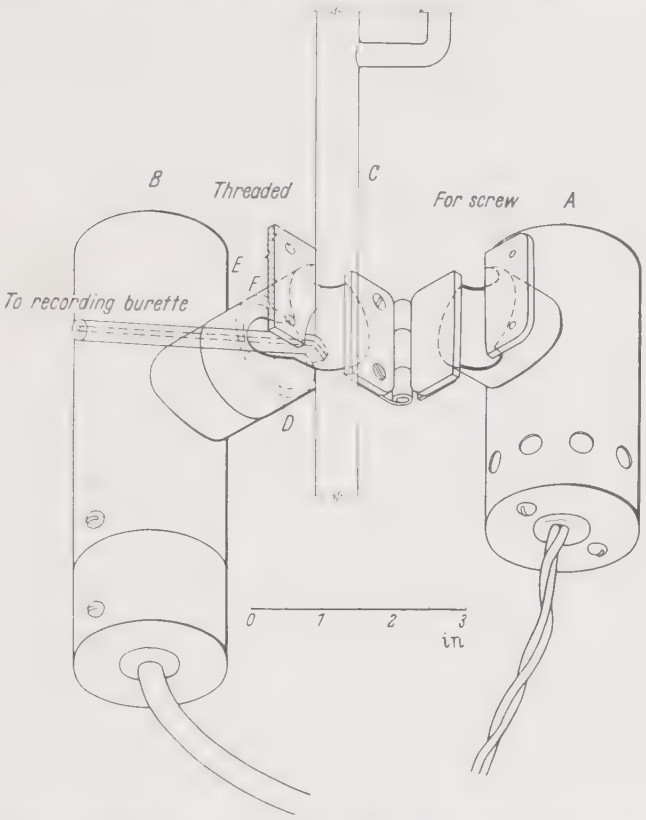

Figure 3. Isometric drawing of photocell and lamp housing with titration cell in position

A, lamp housing; B, photocell housing; A and B made of chromium plated brass tubing (1⅜ inch diameter); C, titration cell with capillary glass tubing (1 mm) leading to the recording burette; D, slot for capillary glass tubing in socket of photocell housing; E, socket for photocell housing; F, darkened window on photocell housing. The unit is made of brass and is hinged so that a section of the titration cell can be completely enclosed when the hinge itself is closed

by removing the photocell housing from its socket. The photocell, as before[1], is the Cintel type VA26T and is operated with 70V at its anode. The lamp is a 12V, 15W, and interposed between the titration cell and the photocell is a darkened window to keep light falling on the photocell to a reasonable value.

This photoelectric control unit has been working continuously for eighteen months, and has required no attention except for the usual replacements. The unit may be more costly than the original, but its high sensitivity and stability more than compensate for the extra outlay.

Automatic switch-off device

The valve-tubing gasket between the chromatograph column and the titration cell occasionally allows indicator solution to leak into the vapour

jacket. Light can then pass directly from the lamp to the photocell, resulting in the carriage moving rapidly across the recording drum until the arm attached to the carriage and burette plunger comes in contact with the gland. Although it is unlikely that this will damage the gland it can easily result in a broken burette, and this occurred on one occasion in this laboratory. To prevent this, and since it was often convenient to leave the apparatus working unattended overnight in order to complete analyses, a device was incorporated which shuts the apparatus down if the gland or burette are in danger of being damaged. This is simply an ordinary electric light switch with an elongated toggle which is mounted on the steel rods supporting the carriage. The power supply passes via this switch to a control panel to which are connected the photoelectric control unit, the electrothermal heating mantle for the boiler of the vapour jacket and the electric clock mechanism driving the recording drum. When the carriage moves a specified distance across the recording drum the edge of it trips the switch and shuts the apparatus down. The switch is easily installed and is a cheap and efficient safety precaution.

Preparation of Sample for Analysis

In biological experiments volatile fatty acids are invariably isolated as their sodium soaps. James and Martin[1] converted the soaps to acids by taking 30 μl of an approximately 2N solution and acidifying with phosphoric acid. The acidified solution was transferred to a micro partition column containing Celite 545 and anhydrous sodium sulphate, and the volatile acids were eluted with ether (approximately 1 ml). The acids are brought on to the chromatograph column in a current of air at 100–150°C. This method has certain disadvantages since it is not always possible to prepare 2N solutions of soaps, and it is difficult to elute the volatile acids quantitatively from the micro partition column. Losses of formic acid, and to a much lesser extent, acetic acid, occur when mixtures containing acids from formic to decanoic are drawn on to the column at 150°C, and the apparatus is not entirely satisfactory even at 100°C. It has recently come to my attention that workers[13] in Holland have independently reached the same conclusion concerning the loss of formic acid. Volatile fatty acid mixtures obtained by steam distillation usually contain higher acids, the soaps of which are not readily soluble in small volumes of cold water. It is possible, however, to overcome this difficulty by carrying out a preliminary separation of the volatile acids by buffered[14] or liquid–liquid partition chromatography[15–17]. This, however, limits the usefulness of the method and results in the loss of formic acid if buffered columns are used. The following procedure for converting soaps to acids and transferring them quantitatively to the chromatograph columns overcomes these difficulties.

An aliquot part of the soap solution containing approximately 2000 μg equiv. of acid is taken to dryness in a small glass reaction vessel (see *Figure 4*) at 100°C. The soap solutions do not have to be made up to any particular strength and are usually ~ 1N. The soaps are acidified with 0·3 ml 8N sodium monohydrogen sulphate and 4 ml of ether is added together with 1 g anhydrous sodium sulphate. The mixture is ground and intermixed by means of a pestle. The dry ethereal solution of the acids is transferred to a

20-ml standard flask by introducing the spout of the reaction vessel into the neck of the flask, and then tipping up the vessel until the spout is vertical. The sodium sulphate is extracted with successive aliquot parts of ether (approximately 1 ml) and the solution made up to volume. If done correctly

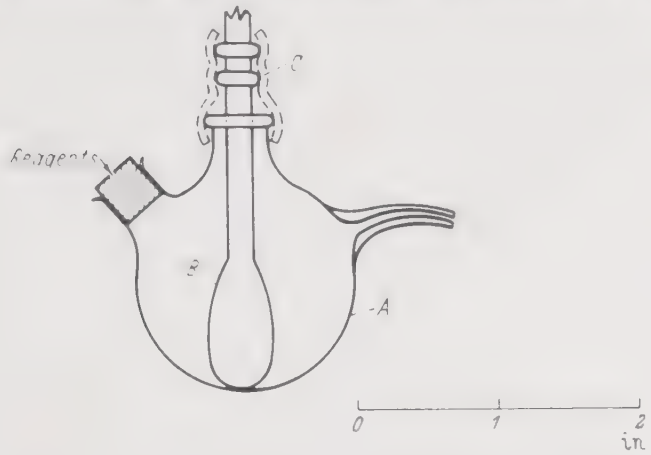

Figure 4. Glass reaction vessel for converting soaps to acids
A, reaction vessel; B, pestle; C, flexible rubber connection

no sodium sulphate should pass into the standard flask. The spout of the reaction vessel is made of 1-mm capillary glass tubing and is curved slightly so that any of the ethereal solution retained in the spout will drain back into the vessel when the spout is horizontal. A further precaution can be taken to prevent loss of volatile acids by connecting the pestle to the reaction vessel with a piece of flexible rubber tubing.

An aliquot part of the ethereal solution of the acids (0·5 ml) is then introduced into the modified chromatograph column (see *Figure 5*) by means of

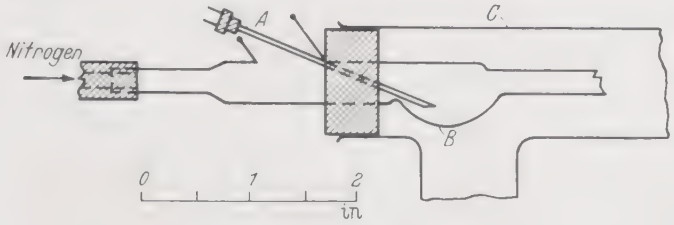

Figure 5. Vapour jacket with modified chromatograph column in position
A, 2-inch stainless steel 'Record' needle fitted to 'Agla' micrometer syringe; B, receptacle with a capacity of 1 ml for samples of acids; C, vapour jacket

an 'Agla' micrometer syringe, fitted with a 2-inch standard 'Record' type stainless steel needle. The chromatograph column was designed initially to take samples up to 1 ml in volume without removing it from the vapour jacket, but it should be possible to modify it to take much larger volumes if necessary. Should the chromatograph column break when being packed, section *B* is cut off and sealed on to another length of glass tubing. Care has to be taken in making the columns, however, since they must fit exactly in the vapour jacket. When the sample has been introduced the stainless steel needle is replaced by a rubber bung, and nitrogen is passed through the column at room temperature until the ether has evaporated. The nitrogen

flow is then reduced until it just bubbles through the indicator solution in the titration cell (approximately 1 bubble/second) and the column is heated to the required temperature. Five minutes after the column temperature has been reached, the nitrogen is turned on again and the analysis started.

The method is quick, quantitative and reproducible and has the added advantage that the chromatograph column does not have to be removed from the vapour jacket. The amounts of the various reagents given above are those most frequently used in this laboratory, but the method can be applied to soap solutions of any concentration. For example, solutions containing only 60 μg equiv. of acetic acid in 10 ml of water have been satisfactorily estimated when only 6 μg equiv. of the acid has been introduced to the column.

Factors Influencing Column Efficiency

It soon became apparent that there was a considerable difference in the effective life of a 4-ft chromatograph column packed with the DC550 silicone/stearic acid mixture of James and Martin[1] when operated at 100°C and 137°C although these workers reported that the only factor limiting the life was breakage. We have never been able to use a column for more than one analysis if operated continuously for 24 hours at 137°C although we have used several hundred over the past two years. Columns run at 100°C, on the other hand, last for several weeks before there is a noticeable deterioration in the resolution of the acids. An important point is that the efficiency must be falling off during the course of an analysis at 137°C and this for obvious reasons is unsatisfactory. It is not possible in the time available to give a detailed account of the results which have accumulated from this phase of the work, and the following discussion will be confined to a few general observations.

Loss of stearic acid from the chromatograph columns

When a chromatograph column packed with DC550 silicone/stearic acid was run continuously at 137°C the indicator solution (0·01 per cent phenol red) in the titration cell became turbid after about 6 hours, due to loss of stearic acid. This interferes with the titration of the higher volatile acids (C_{10} to C_{12}) since sufficient light cannot pass to the photocell, although the indicator solution is acid (yellow). The loss was reduced if the Celite 545, which had been sized and dried in the usual manner, was kept over phosphorus pentoxide for at least 48 hours before use. It would appear that the Celite takes up water from the atmosphere or is not completely dried when heated in an oven at 300°C for 3 hours. The stearic acid (m.pt 69·5°C) presumably steam-distils from the column. It is interesting to note that once the column started losing stearic acid, the rate of loss of acid appeared to increase with time. Since Celite could only take up or retain a limited amount of water, it could be expected that the rate of loss of acid would decrease as the column dried out. It seems likely therefore, that the presence of water is only one of the factors involved, and further work will still have to be done on this problem.

As mentioned above, the resolution of volatile fatty acids on a 4-ft chromatograph column packed with DC550 silicone/stearic acid was drastically impaired when run continuously for 24 hours at 137°C. A similar result was

obtained by heating a fresh mixture of DC550 silicone/stearic acid in an oven for 24 hours at 137 C prior to packing in a column. When DC550 silicone alone was used as the liquid phase, however, the efficiency remained constant for several weeks although the resolution of the acids was not as good as on a freshly prepared column containing the DC550 silicone/stearic acid mixture.

The analysis of heptanoic to decanoic acids, however, can be carried out satisfactorily on DC550 silicone[12]. If the fall in efficiency was due to the loss of stearic acid alone, the retention volumes of volatile acids should decrease until eventually they would be identical to those obtained from a column containing only DC550 silicone as the liquid phase. The retention volumes show no tendency to decrease, however, although the acids are imperfectly separated due to tailing. This suggests that the volatile acids are being adsorbed on the Celite.

It was found that >80 per cent of the stearic acid remained on the column after running for 24 hours at 137 C and the acid was distributed equally along the whole length of the column. Also, if the column packing was removed and the amount of acid lost (i.e. approximately 20 per cent) was added to the mixture, and the column repacked, the efficiency did not improve.

It would appear, therefore, that the presence of stearic acid in the mixture is in some way responsible for the fall in efficiency, since it could be expected that if adsorption was responsible, a column containing only DC550 silicone run under the same conditions should behave similarly. The problem is complex, and although a considerable amount of work has been done on it, there has been no success so far. It is possible, however, that if other materials with lower adsorptive properties than Celite 545 were used as the supporting medium for the liquid phase the difficulty would be overcome.

Liquid phase other than DC550 silicone/stearic acid

During the above work many liquid phases were tried in order to improve the separation of the volatile acids, and in an effort to find a liquid phase that could be used for several analyses at 137 C[12]. They included *o*-tricresyl phosphate, silicones DC720 and DC200, the latter having viscosity grades of 100, 500 and 1000 cS. Varying proportions of monocarboxylic acids (C_{20} and C_{22}) and dicarboxylic acids (C_{13}, C_{18} and C_{20}) were admixed with the silicones. Of these mixtures the most satisfactory separations were obtained using any of the silicones together with 10 per cent arachidic acid (C_{20}) or behenic acid (C_{22}). These acids were not lost from the column at 137 C and the resolution of isomeric acids was improved. The column efficiency deteriorated in the same way as before, but not as rapidly, and it was sometimes possible to carry out two analyses with the same column. Good separations of the volatile acids were obtained when the monocarboxylic acids were replaced by dicarboxylic acids in the liquid phase, but although there was no loss of acid from the column, the efficiency deteriorated to a greater extent at 137 C than with the silicone DC550/stearic acid mixture, and there was the added disadvantage that the dicarboxylic acids had only a very low solubility in the silicones.

On *o*-tricresyl phosphate*, all the acids up to *n*-valeric acid, excluding α-methylbutyric acid, can be separated on a 4 ft column at 100° C. αα-Dimethyl substituted acids show inversion of order on this liquid phase, and are eluted before the *n*-acids with one carbon less. For example, αα-dimethylpropionic and αα-dimethylbutyric acids are eluted before *n*-butyric and *n*-valeric acids respectively. The separation of *n*- and *iso*-acids is superior to that obtained on DC550 silicone/stearic acid, and is such that αα-dimethylpropionic acid is intermediate between *iso*butyric and *n*-butyric acids, and is completely resolved. It is unfortunate, however, that α-methylbutyric acid is incompletely separated from *iso*valeric acid. The retention volumes of the acids are much greater on this liquid phase than on the silicone mixtures, which can be attributed, no doubt, to the strong hydrogen bonding properties of the phosphoryl group($=P^+—O^-$). The behaviour of the αα-dimethyl substituted acids could be explained if the dipole interaction between the permanent $-P^+—O^-$ dipole and the highly polarizable *o*-cresyl nuclei had a tendency to orient these nuclei in a manner which would sterically hinder acids substituted on the α-carbon from forming hydrogen bonds. This is supported to some extent at least by the fact that the retention volumes of these acids relative to their corresponding *n*-acids are affected more than those which are not substituted on the α-carbon. Since this liquid phase can only accept protons, any slight differences in the ability of the volatile acids to form hydrogen bonds will be accentuated. This liquid phase should be useful in the analysis of other types of compounds, such as amines and alcohols, which are capable of forming hydrogen bonds. With the latter, by analogy with the volatile acids, it could be expected, for example, that *tert*butyl alcohol would have a lower retention volume on this liquid phase than *n*-propyl alcohol. This liquid phase can only be used once if operated at 137°C for 24 hours.

Conclusion

Although it was reported in the original method[1] that volatile acids from formic to decanoic could be estimated at 137°C we have never been able to obtain quantitative results for acids above decanoic acid. This is probably due to the fact that our retention volumes for the volatile acids on a 4-ft column (4 mm internal diameter) using DC550 silicone/stearic acid as a liquid phase are almost 100 per cent greater than those reported by James and Martin[1], although the columns contain the same weight of Celite 545 and liquid phase as those of James[18]. A column of the same length, but with an internal diameter of 2 mm packed with only half the usual amount of Celite and liquid phase, gives values identical to those reported[1]. In view of the remarks already made concerning column efficiency at 137°C it is hardly surprising that we have been unable to reproduce their results. It is perhaps significant that the workers in Holland[13], when discussing their modified procedure for the analysis of volatile acids, have only shown results for the acids up to and including decanoic acid. It may be that the automatic

* *o*-Tricresyl phosphate has been used for the estimation of hydrocarbons[19], alkyl halides[20], esters, alcohols and aromatic amines[21] by workers in the U.K., and the author does not claim that his use of this liquid phase is in any respect original. However, as far as he is aware, no one has remarked on the behaviour of αα-dimethyl substituted organic compounds on this liquid phase.

titration method for the analysis of volatile acids should be restricted to the lower acids, and should certainly not be used for quantitative work above decanoic acid.

In conclusion I should like to draw the attention of those attending this symposium to the difficulties scientific workers, who are isolated geographically, have, in interpreting descriptions and diagrams of complex laboratory equipment. This applies to many of the publications on gas liquid chromatography. Unless detailed machine drawings and descriptions of apparatus are given, much time is often wasted in trying to make parts by trial and error, or by relying on helpful correspondence. On the other hand, in the United Kingdom, for example, a short train journey and discussion with others working in the same field can often result in an easy solution to practical problems. Since the publication of methods, results and their interpretation is generally of a very high standard it is possible that practical details and drawings should be published separately in a suitable journal.

I wish to thank Mr J. H. Futter of this laboratory for his help in constructing the apparatus and for his many helpful suggestions, Dr T. R. Pollard and Mr Dromgoolie of the Industrial Development Dept, Canterbury College, Christchurch, for the design and construction of the amplifier for the photoelectric control unit, and the Director of this laboratory, Dr F. B. Shorland, for his encouragement and interest in this work.

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DISCUSSION

H. Boer: I should like to draw your attention to my earlier paper, 'The use of ozonolysis in oil constitution research' *Proc. 4th World Petrol. Congr.*, Section V/A, paper 1, Colombo, Rome, 1955. The survey given there on the GLPC of volatile

fatty acids largely agrees with the author's results. The following data from this paper may be mentioned here.

(*a*) The emerging peaks were detected and recorded using alternatively:
(*1*) a titrating pump and electrically coupled Brown recorder
(*2*) a coulometric titrator and electrically coupled Brown recorder
(*3*) an electrolytic conductivity cell and modified Brown recorder.

Method *3* is very simple, as it requires only a thermostatted 'titration' vessel, containing dilute sodium hydroxide, a conductivity cell and a slightly modified Brown recorder. It can be adapted to other detecting systems (e.g. bases with sulphuric acid, ketones with hydroxylaminé chlorohydrate).

(*b*) The fatty acid sample can be prepared most conveniently by mixing the dry sodium soaps with syrupy phosphoric acid and absorbing the mixture on some Celite that is contained in a detachable piece of the column. This piece is then heated at 150 C in a nitrogen stream and the acids are condensed on the cold column. This method gives low values for formic acid.

(*c*) Factors influencing column efficiency. Better initial efficiency is obtained by dissolving the liquid phase in ether, adding the Celite and stirring to dryness on a steam bath.

Stearic acid was replaced by fatty acids from Carnauba wax (carbon No. ~32). No evaporation of these acids was observed at 137 C. The effective life of the column was somewhat increased. Behenic acid, although better than stearic, was not thought good enough for our purposes. Contrary to your statement about the equal distribution of stearic acid along the column, we found that after a 24 hour run at 137 C, the stearic acid content of the packing at the inlet side of the column had dropped to 84 per cent of its initial value, whereas the content at the outlet remained substantially the same. No migration of the DC 550 was observed. We found that the efficiency of the deteriorated packing could partly be restored by stirring with ether and evaporation to dryness.

Many GLPC separations proceed better on a size-graded fire brick support, for instance, Sterchamol. We found, however, that this brick cannot be used at all for the separation of fatty acids. The same applies to the separation of other highly polar substances like alcohols, unless a liquid phase is used that itself is highly polar, for instance, polyethylene glycol for the separation of alcohols.

I have a final remark for Mr McInnes and some other people who may be interested: I have some reprints of the World Petroleum Congress proceedings.

A. T. James: We never found a marked decrease in column efficiency at either 100 or 137 C; columns were frequently taken from one temperature to another. It is difficult to understand that a column at 100° C should have a life of several weeks whereas at 137 C it has dropped to 24 hours; it is even more mysterious that intermittent operation at 137 C increases the life to 60 hours. Other workers seem to have achieved reasonable results with the method.

We tested a number of methods of obtaining the fatty acids from their sodium salts including the use of packed column sections containing phosphoric acids. The only method giving quantitative recoveries for acids in the range C_1 - C_6 was that described in our original paper. Where formic acid is present it is, however, necessary to lower the time of drawing air through the column to prevent losses.

E. F. Annison: I fully agree with Dr James. When employing a column 11 feet long for the separation of the valeric acid isomers, no deterioration has taken place after 20–30 hours continuous operation.

The methyl ester technique is not suitable for acids lower than C_6 since the esters are too volatile to allow removal of the solvent in which the acids are esterified. I think for acids below C_7, the original Martin technique is obviously very satisfactory, the acids are so simple to detect; but I think to go up to C_{10} or C_{11} is pushing the technique a little far.

A. T. JAMES: I should just like to make a point on that. We recommend for the separation of the fatty acids from C_1 to C_6 or C_8 the use of the titration technique. It is simpler with a much cheaper apparatus, and it gives you readily direct quantitative results in peak areas. But for the remainder of the acids, we separate the range C_5–C_{20} at 200°C with the gas density balance apparatus.

A. R. GRAHAM: Some batches of Celite give poor resolution of the C_1–C_5 fatty acids when using dry nitrogen as carrier. This can be much improved by using nitrogen saturated at room temperature with water as the carrier gas.

We have used a column at 137 C for a week with wet nitrogen as the carrier gas without any falling-off in efficiency.

When a column is first made up, it picks up sufficient moisture to last for about 24 hours when running on dry nitrogen. This may explain the difficulties experienced by Dr McInnes.

Our columns will tolerate a considerable proportion of water in the samples. Thus 20 per cent aqueous solutions of mixed acids are easily resolved and analysed.

A. J. P. MARTIN: I am very interested to hear of the effect of saturating the nitrogen with water and I would like to ask the last speaker if he could tell us how good is the resolution of the acids which it is more difficult to resolve, such as the active and *iso*-valeric acids and the trimethylacetic and normal butyric acids.

P. B. BRINDLEY: In reply to Dr Martin's question the separation of these mixtures has not been investigated, but the separation of normal and *iso*-valeric acids appeared to show an improvement when wet as opposed to dry nitrogen was used on the column at 136°C.

When carrying out rapid analyses it has been found advantageous to use a differentiating recorder in conjunction with the integrated record usually used in the separation of the lower fatty acids. This allows points of inflection on the latter trace to be easily and accurately located.

G. A. P. TUEY: From experience with dinonyl phthalate columns, I should expect that stearic acid itself would disappear at the rate of perhaps 2–3 per cent per hour at 137 C; however, in admixture with silicone, the loss should be very small.

But, using a silicone of foreign origin, we have observed two phenomena which may be relevant. First, a deterioration is apparent during the first 8 or 10 hours use of a new column; after this period, the properties of the column do not change further. This change is due neither to decomposition nor loss of the silicone. Secondly, one of my colleagues has observed considerable degradation of the silicone, with production of volatile products, in the presence of acidic substances. I notice that Dr James mentioned the use of purified stearic acid, and I wonder whether that used by Dr McInnes may have contained a trace of mineral acid.

G. R. PRIMAVESI: We have found that the use of 50 per cent alcohol in the titration cell instead of water (and of course the alkali is dissolved in 50 per cent alcohol) prevents cloudiness and considerably improves the titration of higher fatty acids.

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THE ANALYSIS OF FATTY ACIDS AND FATTY ALCOHOLS BY VAPOUR PHASE CHROMATOGRAPHY

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The pioneer work of Martin and James and of Ray on vapour phase chromatography was limited by the nature of their static liquid phases to temperatures up to about 150 C. During 1953–54 we extended the range of vapour phase chromatographic analysis to temperatures up to 300 C by using silicone grease as the static phase and by building compact column/katharometer units; this apparatus has been used for quantitative analysis of mixtures of methyl esters of straight-chain fatty acids from C_6–C_{22} and for straight-chain fatty alcohols from C_{10}–C_{18}. The method is more reliable, and much more rapid, than previous methods (e.g. the ester fractionation method for fatty acids), and is capable of detecting and measuring small amounts of homologues in the best 'purified' esters and alcohols available.

Many attempts have been made to separate the long-chain saturated fatty acids (or their esters) by chromatography, but no method has been devised which is entirely successful as a quantitative analytical procedure suitable for extensive application. Elution chromatography on adsorbents has always given incomplete separation or low recoveries (Refs 60–77 in Ref. 1). Elution partition chromatography has proved rather more successful, the improved versions of Ramsay and Patterson's method[2] giving good recoveries[3,4]; the reversed phase technique of Boldingh[5] (using benzene as static phase on a synthetic or natural elastomer as support, and a strong polar solvent as mobile phase) gave good separations as the mobile phase was changed in composition[6]. The 'frontal analysis' technique of Claesson[1] gave interesting results on known mixtures of long-chain fatty acids (or their esters) on carbon, but quantitative interpretation of results on 'unknown' samples would be difficult; the displacement development technique[1] did not give quantitative separations when applied to the fatty acids on carbon. Holman with others[7–9] attempted to improve the separations obtainable by displacement development using various displacing agents; subsequently, they tried the 'carrier displacement method' of Tiselius and Hagdahl[10] and succeeded in separating the fatty acids by using a mixture of their esters as the carrier[11]; these methods involve the use of an interferometer (or recording refractometer) to locate and measure the zones. All the methods involving the chromatography of solutions were very time-consuming.

James and Martin[12] separated the fatty acids up to lauric acid by passage through a column of kieselguhr and silicone fluid DC. 550/stearic acid at

137 C (i.e. with a refluxing 2-ethoxy ethanol jacket), and measured each fraction automatically by alkali titration. Ray[13] applied the method to a variety of the lower boiling alcohols, ethers, esters, ketones and hydrocarbons, using dinonyl phthalate (on Celite 545) as static liquid phase, and using katharometers and a high speed recorder for detecting and measuring each component. This communication describes the extension of this technique so that it is generally applicable at temperatures much higher than hitherto, and therefore capable of dealing with the separation and measurement of the methyl esters of the C_{12}–C_{22} fatty acids, and with the C_{10}–C_{18} fatty alcohols; a short account of this work was given by us[14] in 1953.

Experimental

Apparatus

In order to work at relatively high temperatures, the apparatus described by Ray[13] was made very much more compact; the earlier units consisted of a glass helix 25 mm in diameter made from 3 ft of tubing (5 mm in diameter) so as to have about 12 turns with 10–15 mm pitch, with the inlet and outlet katharometers fused on at the top and bottom of the column, as shown in *Figure 1*. Each katharometer consisted of a 100 mm length of fine platinum

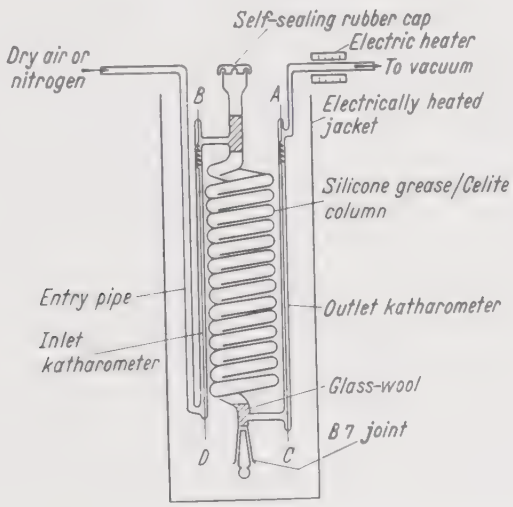

Figure 1. Column and katharometer system (helix)

wire (44 s.w.g.) welded to short lengths of thicker platinum wire (32 s.w.g.), sealed into a narrow glass tube (5 mm in diameter); at the upper end, the 32 s.w.g. wire was coiled, in 6–8 'tight' turns, before being sealed to the glass, so that the coil applied tension to the fine wire. The emergent 32 s.w.g. wires were connected to a Wheatstone bridge arrangement so that the changes in resistance of the outlet katharometer could be recorded on a Cambridge or Sunvic high speed pen recorder, 0–1 mV full scale deflection.

The column/katharometer unit, which was about 40 mm in diameter and nearly 1 ft long, was packed with asbestos flock (with a thermometer bulb embedded centrally) and wrapped in asbestos tape. An iron heating cylinder of 2 inch diameter (closed at the lower end) was wound with 10 coils

of 6 turns each, using Nichrome wire (resistance 9 ohm/yd), the coils being connected in parallel and supplied (via an ammeter) with low voltage from a 25 V mains transformer controlled by a Variac. The cylinder was lagged and bound with asbestos tape. The column/katharometer unit was slid into this cylinder, and the opening was packed with asbestos flock; temperatures up to 300 °C could be reached, and at a given setting of the Variac, temperatures remained steady (±1C°) over many hours.

This apparatus was used for the work on fatty acid esters; during the work on fatty alcohols the katharometers were made more compact by coiling the whole of the 44 s.w.g. wire to give a helix approximately 1 mm in diameter, pitch approximately 0·5–1 mm, omitting the coils in the 32 s.w.g. wire and fitting the whole in shorter glass tubes, e.g. 40 mm long, 5 mm in diameter; the amount of 44 s.w.g. wire was also increased to about 6 inches. The glass columns were made with 3 straight limbs, each 10 inches long (*Figure 2*)

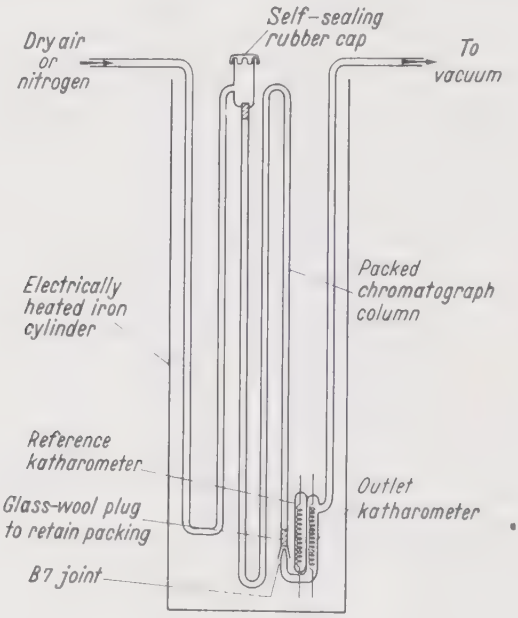

Figure 2. Column and katharometer system (straight)

instead of a helix, thus being both easier to make and easier to fill. It was also found convenient to connect the outlet katharometer by means of a ground glass joint at the end of the column, which also facilitates packing. The inlet katharometer was removed from the inlet pipe, sealed and attached at the side of the outlet katharometer, to avoid thermal e.m.f.'s. The apparatus was fitted with a Hyvac pump, a pressure buffer vessel, a manostat, rotameter and mercury manometers.

The top of the chromatograph column was enlarged and fitted with a self-sealing rubber cap (as used on serum bottles); samples were introduced by hypodermic syringes of 0·05 ml or 0·5 ml capacity, made from glass capillary tubing and 100 mm lengths of 0·5 mm bore stainless steel tubing to serve as 'needles'. If necessary, these were warmed in a flame before use, and low melting samples were melted when necessary. The syringes were graduated

ml 0·01 ml or in cm; for minor components, the amount delivered by a given needle can be made sufficiently constant, but for major components accurate delivery of a fixed volume is not expected, and quantitative work in such cases is normally carried out with an internal standard.

Column packing

The choice of static liquid phase for high temperature work is strictly limited; monocetyl phthalate, octadecyl stearate, paraffin wax, polyethylene succinate, tricresyl phosphate and silicone fluid DC. 703, for example, either charred or slowly distilled out at 250° C. Dow Corning High Vacuum Silicone Grease* appeared most suitable: when 60 g of kieselguhr (Celite 545) was thoroughly mixed in a mortar with 40 g of this grease, a slightly greasy powder was obtained which was quite easily packed fairly evenly in the column, by tapping gently and applying suction at the end. Each filling survives a very considerable number of analytical tests. It has been found advisable to pretreat each bottle of grease as follows: 50 g of grease is stirred with about 50 ml ethyl acetate, diluted with ethyl acetate to about 300 ml and precipitated by adding 300 ml ethanol (74° O.P.); the solvent is decanted off and the grease is washed by decantation with ethanol and dried at 100°C.

The Celite/silicone grease packing gives considerable resistance to flow, so that a 3 ft column with outlet pressure about 2 cm of mercury will have an inlet pressure of about 40 cm of mercury; for work on hexadecanol and octadecanol, in particular, this system necessitated working at about 265°C, which caused slight charring of each 'load' put on to the column and hence a gradual build-up of decomposition products which eventually impaired the efficiency of separation. In order to prevent this, a considerable reduction in temperature was considered necessary, by reducing the resistance to flow so that the inlet pressure would be lower. It was found that sodium chloride, lightly ground and graded between 30 and 60 mesh B.S. sieves, will retain about 5 per cent of its weight of silicone grease, that the mixture can be packed reasonably easily into a column, and so that the inlet pressure would then be about 4 cm of mercury with an outlet pressure of 2 cm of mercury with a flow rate of 4–5 ml (at 760 mm of mercury) per minute. Under these conditions, tests could be carried out at about 60C° lower than hitherto, and thermal decomposition was much reduced.

Results

Fatty acids

Materials—The straight-chain C_{12}–C_{22} fatty acids (even numbers, *Table I*) were converted to methyl esters by refluxing with excess of methanol in the presence of sulphuric acid, and the methyl esters were purified further by

* Since this work was carried out, we have found that E.301 silicone grease from I.C.I. (Nobel Division), Stevenston, Ayrshire, is also suitable and can be used without pretreatment with ethyl acetate/ethanol. E.301 is a very viscous 'gum', and is mixed with Celite 545 or salt as follows: mix the required amount of E.301 with chloroform, added portionwise (e.g. total 30–40 ml $CHCl_3$ per 10 g E.301) and allow to stand overnight (in a stoppered vessel) to complete the dispersion: thin out, if necessary, by adding $CHCl_3$, and pour it into the required amount of Celite 545 or salt, with stirring. Remove most of the chloroform on a steam bath in a fume cupboard, and dry the residue at 130° C. Mix well and transfer to a storage bottle.

partial freezing and pouring away the liquor; the C_{16}–C_{22} esters were also recrystallized from petroleum ether. Subsequently, the esters were analysed by vapour phase chromatography, but for convenience the results on the purified starting materials are given in *Table I.*

Table I. Materials available

Acid	*Source*	*Derived methyl ester*					
		M. pt	*cf. M. pt in Ref. 15*	*M. pt*	*cf. M. pt in Ref. 15*	*VPC analysis ** per cent	*Strength (100 − % impurities)*
Lauric C_{12}	*V. Wolf, Manchester*	—	43·5	5·5–6·0	5	C_{14} 0·5 C_{16} *Trace or nil*	99
Myristic C_{14}	*B.D.H.*	52	54·4	17·5–18	19	C_{12} 3 C_{16} 6·5 C_{18} *Trace or nil*	90
Palmitic C_{16}	*B.D.H.*	64	62·9	29·5–30	29	C_{12} *Trace or nil* C_{14} 2·5 C_{18} 2·2	95
Stearic C_{18}	*Hess Products* 'Distec A.108'	68	69·6	37–37·5	38	C_{14} 3 C_{16} 8 C_{20} *Trace or nil*	89
Arachidic C_{20}	*I.C.I. Specimen Collection*	76·5	75·4	45·5–46·0	45	C_{18} 1 C_{22} >1	98
Behenic C_{22}	*I.C.I. Specimen Collection*	81	80	52–52·5	52	C_{20} ca. 5	ca. 95

* The VPC results were obtained using increased 'load' (0·05 ml) on the column and increased bridge current so that the main component gave more than full scale deflection, and repeat tests were carried out on the esters after enriching with known amounts of the impurities in order to provide calibration data; the temperature was raised to 265°C for arachidate and behenate samples, to produce sharper peaks (see *Figure 3*).

Conditions: calibration using methyl esters—Preliminary trials on mixtures of the methyl esters showed that satisfactory separations were possible with the column at 230° C, with nitrogen flow at 8–10 ml/min, with outlet pressure about 2 cm of mercury, and with a bridge current of 0·2 A; in order to obtain the maximum precision it was considered necessary to adopt the 'internal standard' principle, i.e. a known amount of internal standard would be added to the sample in bulk, about 0·03 ml of the mixture would be put on to the column, and the results would be calculated from the ratios of the heights of the peaks of the various components to the height of the peak of the internal standard, using calibration graphs based on results obtained on appropriate synthetic mixtures. Under the conditions required for separation of fatty

acid esters naphthalene proved to be a useful internal standard, since it gave a sharp maximum on the record at about one minute after addition to the column, well before the next maximum, which is due to methyl laurate.

The results in *Table II* were obtained on synthetic mixtures, the compositions of which were calculated using the purity data in *Table I*; the replicate tests show that reproducibility is of the order of 1–2 units in the value of the percentage figure.

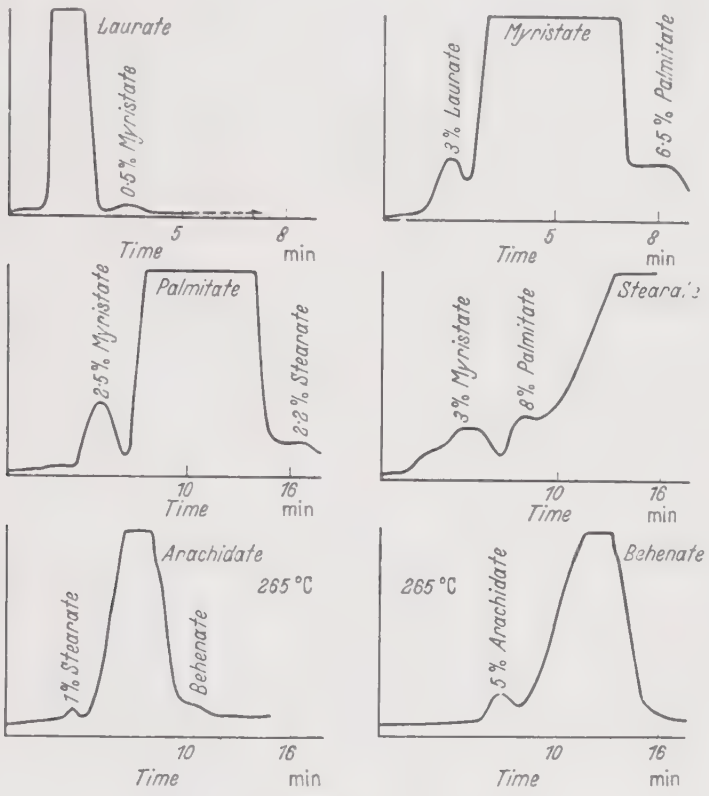

Figure 3. Quality of starting materials

Application to a synthetic mixture of fatty acids—Application of the method as a whole (i.e. including the esterification stage) to a synthetic mixture of fatty acids gave the results shown in *Table III*.

Effect of oleic acid—Under the conditions prescribed, methyl oleate was not separable from methyl stearate, and gave very similar peak heights for equal loads; with fatty acids containing only a few per cent of unsaturated acids, it is probably sufficient to assume that these unsaturated acids consist entirely of oleic acid, to determine iodine value (calc. as oleic acid) of the original sample, and to correct the observed stearate value accordingly.

Application to a sample of isolated 'stearic acid'—Of particular interest at the time this work was carried out was a sample of fatty acids which had been isolated from unsatisfactory aluminium 'stearate', and which had been converted to methyl ester, and fractionally distilled at reduced pressure through a 16 in. × 1 in. column packed with 1/16 in. stainless steel gauze rings. The various fractions were analysed by tests for saponification value

Table II. Calibration Results, using Known Synthetic Mixtures of the Methyl Esters of C_{12}–C_{22} Acids

Item	*Mixture A*				*Mixture B*		
Component C No.*	12	16	18	22	12	16	18
% in synthetic mixture	22	26	25	24	6·2	42·5	48·7
Calculated wt ratio (g ester/1 g naphthalene)	1·39	1·63	1·59	1·5	0·44	3·0	3·43
Observed peak height ratio (ester/naphthalene)	1·11	0·43	0·31	*Not*	0·42	0·92	0·74
	1·02	0·45	0·32	*meas-*	0·48	0·86	0·72
				ured	0·41	0·85	0·65
Mean	1·07	0·44	0·32	—	0·44	0·87	0·71

Item	*Mixture C*			*Mixture D*		*Mixture E*		*Mixture F*	
Component C No.*	12	16	18	16	18	14	20	14	20
% in synthetic mixture	4·3	50·0	43·0	63·0	34·1	16·0	81·0	12·9	83·8
Calculated wt ratio (g ester/1 g naphthalene)	0·35	4·04	3·46	4·66	2·51	1·02	5·15	0·67	4·35
Observed peak height ratio (ester/naphthalene)	0·34	1·06	(0·44)	1·38	0·50	0·55	0·48	0·48	0·53
	0·32	1·18	0·66	1·41	0·51	0·59	0·55	0·42	0·49
	0·35	1·17	0·70			0·65	0·50	0·40	0·40
						0·64	0·49		
Mean	0·34	1·14	0·68	1·40	0·50	0·61	0·50	0·48	0·45

* In each mixture, the minor components (< 2%) have been omitted from *Table II*.

Table III. Application to a Synthetic Mixture of Fatty Acids

Component	Per cent *in acid mixture**	*Ratio of heights ester/naphthalene*		*From calibration graphs*	
		Actual	*Mean*	*Wt ratio ester/naphthalene*	*% Found, calc. as acids*
Myristic acid	13	0·34 0·32 0·32	0·33	0·53	11
Palmitic acid	46	0·69 0·62 0·68	0·67	2·3	48
Stearic acid	41	0·37 0·44 0·38	0·40	2·0	42

* Allowing for impurities in same proportions as given in *Table I*.

[Actual peak heights for naphthalene were 132, 135, 139 mm.]

[0·509 g naphthalene was added to 2·44 g esterified sample.]

and iodine value; with the 'still residues', a correction was made for the amount of unsaponifiable matter present. The sample had given 6 distillation fractions, the first two being myristate and palmitate mixtures, fractions 3 and 4 being palmitate, stearate and oleate (traces), fraction 5 being apparently only stearate plus the bulk of the oleate, and fraction 6 was apparently stearate, arachidate and oleate (traces); the still residue, which comprised nearly 30 per cent of the charge, was apparently good quality *methyl behenate* containing as sole impurity only about 3·5 per cent oleate. When these results were assessed to give the composition of the original sample, it appeared to contain, in addition to lower homologues (see *Table IV*), only 2 per cent arachidic acid and 28 per cent behenic acid. The vapour phase chromatographic method showed that it contained about 35 per cent arachidic acid and only small amounts of behenic acid (*Table IV*).

Table IV. Application to a Sample of Isolated 'Stearic Acid'

Acid	*% w/w calc. as free acids from distillation and analysis of fractions*	*Vapour phase chromatography*		
		Ratio of heights ester/naphthalene (duplicate tests)	*Wt ratio ester/naphthalene (mean)*	*% Found, calc. as free acids*
Myristic	8	0·34 0·45	0·6	8
Palmitic	33	0·63 0·7	2·3	30
Stearic	27	} 0·38 0·37	1·9	25
Oleic	2			
Arachidic	2	0·30 0·24	2·7	35
Behenic	28	(*Small*)	—	—
		[Actual peak heights for naphthalene: 104, 145 mm.]	[0·327 g naphthalene was added to 2·525 g ester.]	

This discrepancy arose because the still residue gave a saponification value corresponding closely to that of methyl behenate; vapour phase chromatography of this still residue gave a record with 4 peaks and 2 inflections [*Figure 4*(b)] *a–f*, of which *a*, *c*, *e* and *f* correspond to laurate, palmitate, arachidate and behenate; myristate and stearate would have given maxima as indicated [*Figure 4*(b)] *b*, *d* and since it is likely that they are in fact present, it can be concluded that the myristate and stearate maxima have been converted into inflections closer to *c* owing to interference by an unknown component which is contributing to the record in the region of *b*–*d*. This unknown component may be a product formed during distillation; it is also possible (and indeed probable since the saponification value is high) that the still residue contains an ester boiling even higher than the behenate, and which would appear only as a slightly raised base line at times far longer than required for behenate. This work reveals the weakness of the ester fractionation method, which in addition to giving the wrong indication as to the behenate content, failed to reveal the large amount of arachidate.

James and Martin[12] showed that the retention volumes of members of a homologous series increased by a constant factor for each additional CH_2

group. In the present work the time at which a particular ester gave its maximum on the record was a function of the number of carbon atoms per

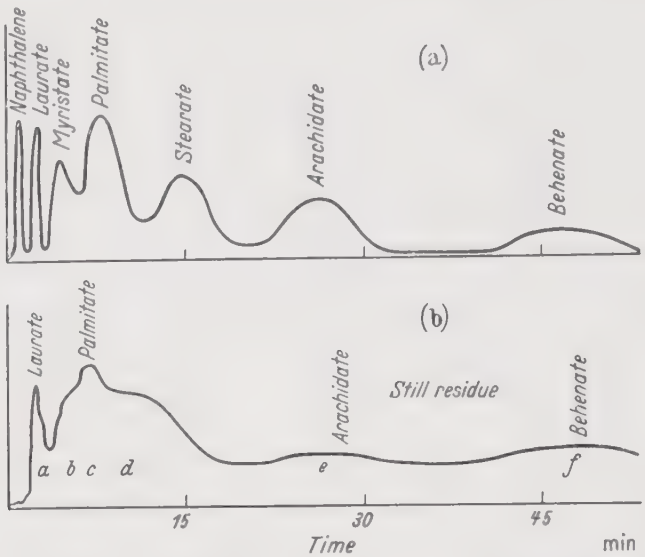

Figure 4. (a) *Synthetic mixture* C_{12}–C_{22} *methyl esters;* (b) *still residue from ester fractionation method*

molecule; this is evident from the following results (*Table V*), which conform to the straight line relationship

$$\log T = a + bN$$

where T is the time at maximum in minutes, N is the number of carbon atoms per molecule of parent fatty acid, and a and b are constants depending on temperature, pressures and flow rates. In this particular 'run' a is $\bar{2}{\cdot}87$ and b is 0·128.

Table V

Component	N	*Observed time at maximum* T min	*Time calculated from* $\log T = \bar{2}{\cdot}87 + 0{\cdot}128\,N$ min
Laurate	12	2·65	2·55
Myristate	14	4·6	4·6
Palmitate	16	8·3	8·28
Stearate	18	15·2	14·9
Arachidate	20	27	26·9
Behenate	22	48–49	48·5

This relationship provides a useful means of confirming the identity of the purified components used in the work on synthetic mixtures, since if a 'purified' sample is incorrectly assigned a certain name, the time at which its maximum appears will reveal the error. Thus it is certain, for instance, that the so-called methyl arachidate sample used in establishing the time for the

arachidate maximum was in fact arachidate and not behenate, from which follows the certain identification of arachidate (not behenate) in the sample of isolated 'stearic acid'.

The ester fractionation method requires a considerable quantity of sample, the distillation stage is a very lengthy one, and the subsequent testing of individual fractions is tedious; on the other hand, the vapour phase chromatographic method can be carried out on a few grammes of fatty acid (for the preparation of quite a small supply of methyl ester), the tests can be carried out in triplicate (for example) in a much shorter time, and the apparatus can be used continuously for one sample after another without cleaning or repacking. For routine testing purposes, therefore, the vapour phase chromatographic method offers outstanding advantages, arising partly from the scale on which the test is carried out and partly from the unique nature of the process, which contributes to the speed and ease of testing routine samples; in addition, the chromatographic method will reveal traces of homologues in almost pure materials (see *Figure 3*, results in *Table I*).

Fatty alcohols

Materials—The straight-chain fatty alcohols (C_{10}–C_{18}, even numbers) were purified by distillation, and the middle cuts were recrystallized from acetone; each final product was ultimately found to be free (i.e. < 0·5 per cent) from homologues by the vapour phase chromatographic method.

Conditions—The technical products of interest in this work were (*a*) relatively good quality dodecanol, tetradecanol and hexadecanol, and (*b*) crude lauryl alcohol containing about 2 : 1 dodecanol/tetradecanol. The chromatographic work was therefore of two kinds: (*i*) determination of traces of homologues in the good quality alcohols, and (*ii*) determination of homologues and of the two major components in the lauryl alcohol; the work on dodecanol and tetradecanol, and on lauryl alcohol, was carried out on Celite 545/silicone grease columns at 230 C, with outlet pressure 2 cm of mercury and flow rate 8 ml/min; tests were also carried out under these conditions (but at 240 C) on hexadecanol/octadecanol mixtures, but for the reasons given above, the Celite 545 was replaced by graded sodium chloride (carrying 5 per cent of its weight of silicone grease) which reduced the resistance to flow to such an extent that 2 cm of mercury outlet pressure gave 4 cm of mercury inlet pressure, with flow rate 4–5 ml/min. Under these conditions, tests were carried out on hexadecanol/octadecanol mixtures at 195–210 C; it was found that 5 per cent of octadecanol gave a definite peak, and it was evident that the limit of detection would be of the order of 1–2 per cent of this alcohol. When only the minor homologues were required, the 'load' (about 0·05 ml) put on to the column was kept as constant as possible by careful measurement in the hypodermic syringe, and the amounts used were such that each minor component gave a suitable peak, although the major component gave more than full scale deflection; when the major component was required, in crude lauryl alcohol, decanol was added as internal standard, and the 'load' was reduced to approximately 0·02 ml.

Small amounts of homologues in tetradecanol and in hexadecanol—*Table VI* exemplifies the method when applied to the determination of small amounts of dodecanol and hexadecanol in good quality tetradecanol; the two synthetic

mixtures, which provide the calibration data, cover the range 1–5 per cent of each homologue. The reproducibility is about ± 0·2 unit in the percentage value.

Table VI. Analysis of a Sample of Technical Tetradecanol

Component	Per cent *in synthetic mixture with tetradecanol*	*Peak heights*		*Notes*
		Actual mm	*Mean*	
Dodecanol	3·7	55 54 57	55	
Hexadecanol	5·1	43 45 48	45	
Dodecanol	2·3	27 29 24	27	
Hexadecanol	3·2	25 27 27	26	
Technical tetradecanol C_{12}	—	52 52	52	=3·6% *dodecanol* *in the*
Technical tetradecanol C_{16}		11 11	11	=1·5% *hexadecanol* *sample*

The conditions can, of course, be varied considerably to suit different applications; thus, the salt/silicone grease column can be used for higher percentages of octadecanol, with different 'loads' and column diameters. *Table VII* shows results for octadecanol in a technical sample under various

Table VII. Results for Octadecanol in a Sample of Technical Hexadecanol, under Various Conditions

Column bore mm	*'Load'* ml	*Column temp.* °C	*3 Synthetic mixtures*		*Sample of technical hexadecanol*	
			C_{18} per cent	C_{18} *Peak height* mm	C_{18} *Peak height* mm	*Octadecanol in sample* per cent
10	0·5	210	5	65	87	7
5	0·02	190	30	58	17	9
6	0·05	205	23	170	65	9

Table VIII. Homologues in a Sample of Crude Lauryl Alcohol

Component	Per cent *in synthetic mixture with dodecanol*	*Peak heights* mm	*Notes*
Decanol	3·0	8 7	
Tetradecanol	28·2	27 27	
Sample of technical dodecanol C_{10}	—	7	= 3% *decanol* *in the*
Sample of technical dodecanol C_{14}		28	= 28% *tetradecanol* *sample*

Table IX. Dodecanol Content of a Sample of Crude Lauryl Alcohol

	Wt ratio taken C_{12} C_{10}	*Peak height ratios* C_{12}/C_{10} *Actual*			*Mean*	*Observed wt ratio (from calibration)* C_{12}/C_{10}	*Wt decanol present* g	*Dodecanol* *Wt* g	%
Column temperature 222 C									
Synthetic mixtures C_{10} *and* C_{12}	1·19	1·20		1·19	1·20	—	—	—	
	1·44	1·35		1·35	1·35	—	—	—	
	1·01	1·07		1·06	1·07	—	—	—	
Sample of lauryl alcohol	0·353 g *decanol added to* 0·678 g *sample*	1·21		1·21	1·21	1·22	$0{\cdot}353 + \left(\frac{3 \times 0{\cdot}678}{100}\right)$ = 0·373	0·455	67
	0·449 g *decanol added to* 0·725 g *sample*	1·085	1·095	1·085	1·09	1·03	$0{\cdot}449 + \left(\frac{3 \times 0{\cdot}725}{100}\right)$ = 0·470	0·485	67
Column temperature 225 C									
Synthetic mixtures C_{10} *and* C_{12}	1·19	1·19	1·20 1·21	1·23 1·25	1·22	—	—	—	
	1·44	1·33	1·33 1·35	1·36 1·36	1·34	—	—	—	
	1·01	1·13	1·13 1·13	1·14 1·13	1·13	—	—	—	
Sample of lauryl alcohol	0·353 g *decanol added to* 0·678 g *sample*	1·26		1·25	1·25	1·26	*As above* (0·373)	0·470	69
	0·449 g *decanol added to* 0·725 g *sample*	1·14	1·14	1·18	1·15	1·05	*As above* (0·470)	0·495	68

conditions, although we do not advocate the use of such large loads as 0·5 ml. or of synthetic mixtures of composition so greatly different from that of the material under test.

Analysis of crude lauryl alcohol—The analysis of crude lauryl alcohol consists of two parts: the decanol (and tetradecanol) contents were determined by comparison with a synthetic mixture of similar composition, using a carefully controlled load of about 0·02 ml (*Table VIII*), and the dodecanol was then determined using added decanol as an internal standard (allowance being made for the small amount of decanol originally present) and reference to calibration data on dodecanol/decanol mixtures (*Table IX*).

Thus this sample of lauryl alcohol contained 3 per cent decanol, 68 per cent dodecanol and 28 per cent tetradecanol, total 99 per cent. The reproducibility is about ± 1 unit in the percentage value for the major components.

The vapour phase chromatographic tests for quality of the saturated fatty alcohols are more reliable and critical, and very much more rapid, than the classical distillation method.

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Discussion

A. J. P. Martin: I should like to make a few remarks on the subject of reducing the pressure at the exit end of the column. I think there is very considerable confusion on this subject and I feel that Dr Cropper's remarks are a trifle misleading. James and I described in our first paper the relationship between the inlet and outlet pressures and the retention volumes. Essentially the rate of movement of the zone is dependent on the linear velocity of the gas and there is a constant R_F independent of the local pressure of the carrier gas. The only difference between the liquid–liquid column and the gas–liquid column is that the gas velocity varies down the column. James and I showed that the assumption of uniform packing along the length of the column gives an excellent agreement with the results of experiment. In general I conclude that there is no advantage in reducing the pressure in the column, except for certain pieces of apparatus where special conditions may reign. I fear that

Dr Cropper's advocacy of low exit pressures, no doubt desirable in his special conditions, should not be taken as a general recommendation.

A. T. James: I should like to make one or two comments on the degree of resolution shown in the separations by Cropper and Heywood of long-chain fatty acids. If one compares the behaviour of the long-chain fatty acids on their silicone grease stationary phase with Apiezon M one finds that on the silicone grease the separation factors are perceptibly lower, so that in fact, for fine resolutions, it is a poor stationary phase. I think my rough calculation from the figure gives a 2-CH_2 group separation factor of about 1·8, whereas on an Apiezon M column at 200 C the separation factor is 2·32 for the 2-CH_2 group, 1·54 for 1-CH_2 group, which, with a reasonably high efficiency column, will give you very fine resolution even of the unsaturated fatty acids.

Also I believe it to be quite impossible to pack a spiral glass column and get a reasonably high efficiency out of it. If one must have a spiral column, then the technique used by Dr Keulemans and his group of packing copper or other metal columns in a straight length and then coiling will give you much higher efficiencies. The glass spiral cannot be vibrated in general without shattering it, and vibration is most important. I emphasize that proper packing of the column is of the first importance. It is a pity to throw away the capability of the resolving power of columns by not packing correctly. Packing done only by light tapping will not take in much materials of support and stationary phase; consequently retention will tend to be low. If one wishes to do this with a properly packed column, it is necessary, of course, to drop the amount of the stationary phase relative to the amount of support. Even with amounts some 30 per cent of those I reported in my recently published paper on the long-chain fatty acids, columns still have a high efficiency, and retention volumes can be reduced by a factor of two. This is useful when carrying out a large number of separations. Using Celite 545/Apiezon M columns (10 g to 2 g) at 200 C the range C_8–C_{19} can be covered in $2\frac{1}{2}$–3 hours. Arachidonic acid is too slow under these conditions, but should be capable of being run at a temperature of 250°C using Apiezon L as stationary phase.

A. Heywood: With respect to the spiral column, we no longer use that now. The column is now a three-leg arrangement and is much simpler to fill.

With respect to packing the column, there is a paper by Littlewood where he showed that, irrespective of the actual length of the column, the corrected retention volume is constant. We do not find it makes a lot of difference. We have had columns operating quite satisfactorily with 2 cm gaps and with no apparent effect on the separation of our gases.

F. R. Cropper: I did not claim, Dr Martin, that we get improved separation at reduced pressures. I admitted in the paper that you may well get improved resolution at atmospheric pressures.

However, I would like to ask Dr James how he would proceed to determine 1 per cent of stearate in arachidate as we have done?

A. T. James: I think I made the point that the columns I have described cover the range from C_5 to C_{19}. They do not cover the range to C_{22} for which one needs a temperature higher than 200°C, possibly 250°C.

R. P. W. Scott: Concerning the effect of packing spiral columns, I must agree with Dr James when he says that you cannot obtain the same efficiency from the spiral columns as you can from the same length of straight column. However, you can improve the efficiency of packing spiral columns in their spiral form if you reduce the quantity of liquid phase on the support and pack with a throughput of gas greater than that used under operating conditions and with light vibration.

One can obtain from a given column in spiral form an efficiency of 1200 theoretical plates whereas the same length of column in the straight form has 1600 plates.

There is one other point: a speaker said he saw no change in the retention

times when he had gaps in his column. I agree with the fact that the retention time is only proportional to the quantity of liquid phase, but there is a big difference between the retention time and resolution; the retention time is only half the story.

L. Blom: I am a little astonished at the remarks about the spiral columns. Most of my columns are spirals and I compared them with straight columns; I never saw a significant difference in the resolution of these columns. If you apply suction during the filling of the column, I think the column is as good as a straight one.

A. Klinkenberg: I was interested to hear the statements about the possible effect of the coiling of columns and the disagreement of opinion thereon. Now it occurred to me that if a column is coiled with a rather small radius of coil, there should of course be an effect, the idea being that the pressure difference available between two cross sections must be constant, and the outside path is longer than the inside one, so that we get a lower velocity on the outside. We really get *this* effect twice because the outer circle is longer than the inner circle and is followed at a lower velocity. So that 10 per cent difference in radius would actually give 20 per cent difference in velocity. One would expect that peaks would be smeared out at the end of the column and spread out over a distance of 20 per cent of the retention volume.

Now, of course, nothing of the sort happens and this must be attributed to radial mixing between the liquid going slowly in the outer region and the gas going more quickly in the inner circle. They must mix radially enough to give a reasonable resolution at the end. But this is bound to be affected by the ratio of radius of coil to radius of tube, and I wonder if anything could be said about the influence of the variation of this ratio of coil radius to tube radius. Perhaps Dr Blom has been in a very favourable position in having rather wide coils of rather narrow tube.

E. Glueckauf: I am afraid I must come to the rescue of the spiral column. The situation that the gas comes round the outside slower than the inside just does not arise, because not only have we a considerable diffusion effect in the longitudinal direction, but fortunately, in this case, we also have one which goes transversely to the column and which almost eliminates the whole feature of which Dr Klinkenberg is afraid. There will be a small effect resulting in an increase of theoretical plate height, but it is only a small proportion of the effect which is produced by the longitudinal diffusion.

A. Klinkenberg: I do not think I succeeded in making myself quite clear as to what I wanted to say a little while ago. The idea was that if there were a constant pressure difference between two cross sections, thereby giving a linear flow rate decreasing from inside to outside and, moreover, if the paths were increasing from inside to outside so that the times were greatly different, then of course, if there were no interaction between the different circles and there were 10 per cent or 20 per cent time difference between the two circles, inside and outside, peaks would be spread out at the end of the column over 20 per cent of the total holding time. From that I concluded that there must be an interaction between the streams at different distances from the axis of the coil and radial diffusion.

I think this is specifically the point Dr Glueckauf raised in his reply, but I think we agree to that already. My only problem was how we were going to understand quantitatively.

E. Glueckauf: I am not going to calculate it!

A. J. P. Martin: I should just like to remark here that Dr Glueckauf's defence of the spiral column is, I think, somewhat conditioned by the fact that most of the absorbents he has used have permitted rather free diffusion in all directions. The degree of freedom of diffusion which occurs in different types of packing is very great. In the Celite type of column particularly where, using high proportions of liquid phase, the diffusion from one side to another is difficult and, in fact, the longitudinal diffusion is so difficult that one seldom notices any decrease in efficiency as the rate is slowed down to any practical value, under the same low rates of flow.

increasing the diffusivity by replacing nitrogen with hydrogen will increase the efficiency of the column, showing that sideways diffusion is a limiting factor. Obviously, if you had a column of that type, then this effect Dr Klinkenberg mentioned is likely to be important. If one is using a very open packing of the type that Dr Keulemans uses, then of course it is very much less important.

F. VAN DER CRAATS: We investigated the influence of coiling on column efficiency. The plate number of metal columns of 3, 6 and 12 mm diameter was determined with straight tubes and tubes which had been coiled to various radii. With 30 per cent wt of silicone oil on Sterchamol 50–70 mesh and nitrogen as carrier the effect of coiling was very small as long as the ratio of the radius of the coil to the diameter of the tube was greater than 10. At a ratio of 5 a loss in plate number of 15–20 per cent was measured. At gas velocities considerably above the optimum velocity this effect is much larger.

With hydrogen as carrier the loss in plate number was about half that measured with nitrogen.

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VAPOUR PHASE CHROMATOGRAPHIC ANALYSIS OF CHLORINATED HYDROCARBONS AND HYDROCARBON GASES

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Vapour phase chromatography has been found to be a most powerful tool for the analysis of complex mixtures of chlorinated hydrocarbons and mixtures of light hydrocarbon gases. For liquid samples the apparatus used is substantially as that described by Ray. Retention volumes of some thirty compounds have been determined using a number of stationary phase liquids. Of these, tricresyl phosphate, 'dinonyl' phthalate and Silicone MS 710 have proved to be the most useful. Gas mixtures are analysed on a 25-ft liquid paraffin column maintained at 0° C, hydrogen being used as carrier gas. Methane, ethane, ethylene, propane, propylene and carbon dioxide may be determined, but air interferes with the determination of methane. A number of factors, including the temperature of injection and the katharometer wire and block temperatures, have been studied to find their effect on the accuracy of the method.

During the last two years vapour phase chromatography has become established as one of the most powerful techniques available for the analysis of a wide variety of compounds. It has been found to be particularly valuable for the identification and estimation of impurities in chlorinated hydrocarbons and in light hydrocarbon gases.

1. Analysis of Chlorinated Hydrocarbons

The apparatus used for the analysis of liquid mixtures of chlorinated hydrocarbons is substantially as that described by Ray[1]. The W-shaped columns, 1800 mm × 4 mm, heated by horizontal vapour jackets, are packed with size-graded Celite 545 and stationary phase (10 g to 4 g) by a combination of air pressure and vibration. From the carrier gas flow diagram (*Figure 1*) it will be seen that the katharometer is connected, by short lengths of 1-mm internal diameter stainless steel capillary, to two columns, gas passing simultaneously through both to a common pumping system. The two two-way taps allow the flowmeter to be connected in circuit with either column at will, the other column then providing a reference gas stream. This arrangement greatly facilitates changing from one type of column to another without delay due to warming up, etc. It is preferred to the method described by Callear and Cvetanovic[2] since no taps are needed between the end of the column and the thermal conductivity cell. Any possibility of

contamination is thereby eliminated and the 'dead-space' may be reduced to a minimum.

The katharometer is constructed from a $5\frac{1}{2}$-inch length of 3-inch diameter copper bar; the wires, 4 inch × 0·001 inch, being mounted in $\frac{5}{16}$-inch channels as shown in *Figure 2*.

The copper lead-in wires (*ca.* 30 s.w.g.) are soldered to the ends of the 1-mm internal diameter steel capillaries, cemented (by glycerin–litharge mixture) into glass insulating sleeves in the threaded bushes. One lead-in wire for each

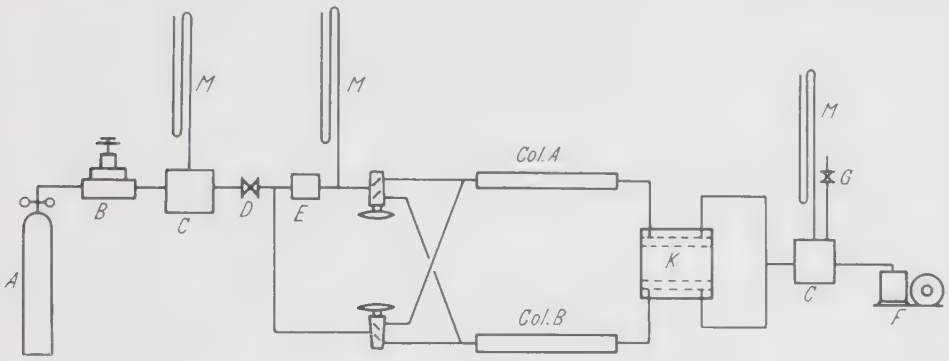

Figure 1. Carrier gas system

A Gas cylinder *D Needle valve* *G Air leak*
B VPC1 controller *E Flowmeter* *K Katharometer*
C Buffer vessels *F Pump* *M Manometer*

cell is formed into a small spring whilst the other is bent at right angles to allow the fine platinum wire to run on tangentially. Before assembly the two platinum wires are adjusted to equal length (within 0·2 per cent) by measurement of their electrical resistance in a bridge circuit. The wires are mounted under a tension of 10 g, the spring taking up any expansion on heating.

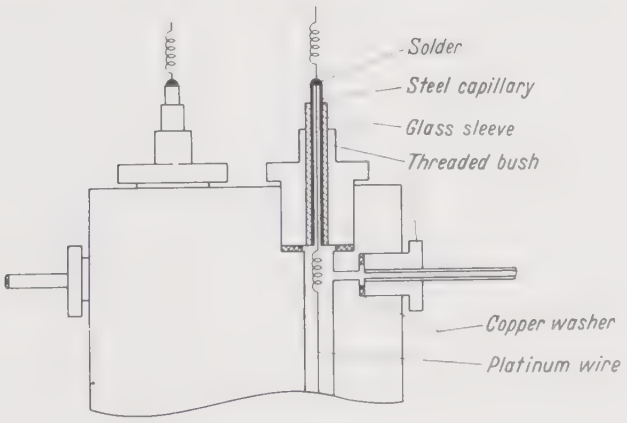

Figure 2. The katharometer

Several katharometers of this type have been made and it has been found that they have a very stable zero and are completely insensitive to vibration. Ediswan metal–glass seals (Type 3312) have been used recently in place of the cemented assembly, a modification making the katharometer more suitable for high temperature applications.

The wires form two arms of a d.c. Wheatstone bridge, powered by a large capacity 12 V accumulator, the out-of-balance p.d. being fed directly to a 10 mV Honeywell–Brown recording potentiometer (Type 153 X 12). Provision is made in the circuit for control of bridge current, sensitivity and zero, as shown in *Figure 3*. The reversing switch is incorporated to allow the record

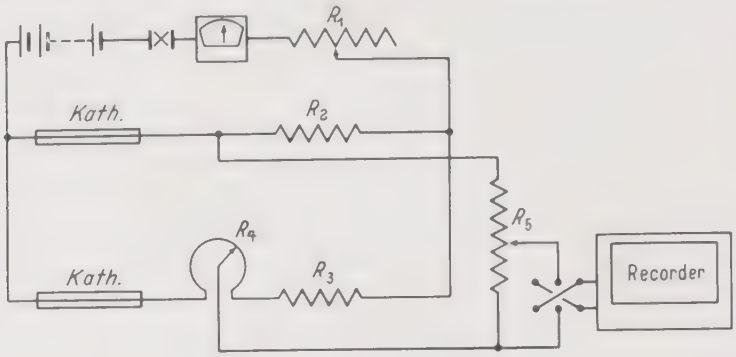

Figure 3. Electrical circuit

R_1 10 ohm *Helipot* R_4 1 ohm *Muirhead A2A (Zero)*
R_2, R_3 30 ohm *Constantan* R_5 1000 ohm *Decade (Sensitivity)*

to be run from the same zero irrespective of which column and cell is being used.

If the sensitivity control is to be used during the course of a separation, for example, to bring an otherwise 'off scale' peak back on scale, it is necessary to make the base line of the recording correspond to the electrical zero of the recorder. In order to detect any 'negative' peaks (e.g. water) it is usual to run the base line about 1 inch from the edge of the chart, and it is then necessary to have the electrical zero 'set up' by about 10 per cent.

Stationary phase liquids

The characteristic 'retention volumes' of a number of compounds have been determined using a variety of stationary phase liquids. These include liquid paraffin, Silicone Fluid MS 710, 'dinonyl' phthalate (DNP), tricresyl phosphate (TCP), Arochlor 1248 (a chlorinated diphenyl), Seekay wax R 68 (a chlorinated naphthalene), glycerol, glycol and a solution of silver nitrate in glycol. For the separation of the chlorinated compounds studied TCP, DNP and Silicone Fluid MS 710 have been found the most useful and the bulk of our work has been done with such columns. With the exception of liquid paraffin the other liquids listed proved to be quite useless for the analysis of the mixtures encountered.

Procedure

To avoid leakage from the injection serum cap the nitrogen inlet pressure is maintained at 1–2 cm of mercury positive, the pressure drop across the column being taken up by the pump system. This pressure drop varies for different columns at different temperatures, ranging from 15 cm of mercury for TCP at 35 C, to 26 cm of mercury for Silicone Fluid MS 710 at 77 C. Normally an indicated gas flow rate of 10 ml/min is used but, since the Rotameter (Type 100, calibrated 5–50 ml/min nitrogen at s.t.p.) does not operate under s.t.p. conditions, this corresponds to about 9·3 ml/min at s.t.p. Column temperatures of

35 C (ether vapour), 77 C (carbon tetrachloride vapour) or occasionally 135 C (xylene vapour) have been found suitable for the compounds studied. The detector bridge current is controlled at 240 mA and the katharometer block temperature at 30 C. Sample volumes of 5–50 μl are used, introduced by means of an 'Agla' micrometer syringe fitted with a 2-inch needle. The head of the column is well inside the close-fitting vapour jacket and it has not been found necessary to use a 'vaporizer' or 'flash' heater on the column neck, as described by Bradford *et al.*[3] For quantitative work internal standards are used whenever possible to eliminate errors of sample measurement and the effects of slight variations in operating conditions.

Results

Table I gives the retention volumes of a number of compounds obtained with four types of column packing, liquid paraffin, silicone fluid, DNP and TCP, at temperatures of 35 C and 77 C. These values are the observed retention volumes, determined under normal operating conditions, corrected for 'dead-space' but not for the pressure drop ratio P_1/P_0. The practice, recommended by Littlewood, Phillips and Price[4], of reporting results as 'corrected retention volumes per gram of stationary phase, *V*/*g*', has not been followed, since it has been found that the observed retention volume is affected by the temperature of injection. It is felt that until column operating conditions can be more rigorously defined and controlled, these corrected volumes cannot be used as absolute values.

Keulemans, Kwantes and Zaal[5] have discussed the effect of the stationary phase and have shown that it is possible to control the process of separation by a suitable choice of base liquid. Working with a somewhat heterogeneous collection of chemical types it has not been found possible to establish any broad generalizations but specific examples of the selective effect of the base liquid may be seen from *Table I*. Of particular note is the large increase of retention volume of ethanol, *cis*-1:2-dichloroethylene, chloroform and 1:2-dichloroethane when using the polar liquids TCP or DNP, compared with the non-polar liquid paraffin or Silicone Fluid MS 710. On the other hand many compounds, e.g. ether, 1:1-dichloroethylene, *iso*propyl chloride, carbon tetrachloride, etc., show little variation of retention volume over the different stationary phases.

In this connection it is of interest to consider the work of Hoare and Purnell[6]. From both theoretical considerations and experimental evidence these workers have proposed a logarithmic relationship between retention volume and vapour pressure for members of homologous series and other series of related compounds, applicable over a wide range of temperature.

For a homologous series this appears to be a useful extension of the earlier work of James and Martin[7] and Ray[1], who found a logarithmic relationship between retention volume and chain length.

In support of their theory Hoare and Purnell cite data for two chloromethanes, chloroform and carbon tetrachloride, using a liquid paraffin column at temperatures from 20–110 C. We have found that, owing to the selective effect of the stationary phase, the relationship does not hold for the three chloromethanes, dichloromethane, chloroform and carbon tetrachloride, when using the polar columns DNP or TCP, there is in fact a

Table I. Retention Volumes

Column		Paraffin		Silicone Fluid MS 710		DNP		TCP	
Compound	B. pt °C	35°C	77°C	35°C	77°C	35°C	77°C	35°C	77°C
Ethyl chloride	12·2	72	—	100	—	156	—	130	—
2-*Chloropropene*	22	—	—	132	32	192	44	130	30
iso*Propyl chloride*	35·5	160	48	188	44	276	76	192	44
1:1-*Dichloroethylene*	37	212	56	212	52	325	84	216	60
Dichloromethane	40·1	196	56	332	80	595	136	530	125
Allyl chloride	44·6	212	56	292	76	450	116	370	84
n-*Propyl chloride*	47·2	268	72	308	76	450	116	330	84
trans-1:2-*Dichloroethylene*	48·4	356	96	372	84	590	136	460	110
tert*Butyl chloride*	51·5	268	72	264	64	408	100	260	64
1:1-*Dichloroethane*	57·3	356	96	500	112	840	188	685	150
cis-1:2-*Dichloroethylene*	60·1	452	124	685	148	1320	270	1180	250
Chloroform	61	580	144	775	164	1620	320	1520	290
Propargyl chloride	65	224	60	470	108	—	—	—	—
sec*Butyl chloride*	68	544	144	560	124	870	210	590	136
iso*Butyl chloride*	68·9	—	—	—	156	—	220	—	159
1:1:1-*Trichloroethane*	74·1	780	204	840	176	1290	270	950	200
Carbon tetrachloride	76·5	960	248	940	196	1180	270	980	205
n-*Butyl chloride*	78	780	204	865	180	1380	280	880	190
1:2-*Dichloroethane*	83·5	712	180	1200	250	1780	410	2100	410
tert*Amyl chloride*	86	—	—	880	184	1500	300	920	195
Trichloroethylene	87	—	352	—	290	—	510	—	390
iso*Amyl chloride*	98·9	—	372	—	290	—	520	—	335
1:1:2-*Trichloroethane*	113·5	—	580	—	680	—	1350	—	1350
Tetrachloroethylene	121·2	—	220*	—	—	—	—	—	—
1:1:1:2-*Tetrachloroethane*	130·5	—	—	—	1140	—	—	—	—
1:1:2:2-*Tetrachloroethane*	146·3	—	460*	—	2200*	—	—	—	520*
Ethyl ether	34·6	156	44	160	35	220	55	135	35
Ethyl bromide	38	208	50	265	60	360	88	280	70
Acetone	56·5	108	32	245	60	390	90	440	100
Methyl alcohol	64·7	—	—	70	—	230	—	—	—
n-*Hexane*	69	600	—	—	—	440	—	—	—
Ethyl alcohol	78·9	192	50	160	30	510	88	690	125
Toluene	110	—	670	—	—	—	—	—	—
1:2-*Dibromoethane*	131	—	—	—	980	—	1620	—	—

* At 136°C

reversal in the order of emergence of chloroform and carbon tetrachloride. This is possibly to be expected on consideration of the polarity of the solvent and the polar nature of chloroform, as compared with carbon tetrachloride. With the relatively non-polar Silicone Fluid MS 710 as base liquid the Hoare–Purnell relationship appears to be approximately obeyed.

All the compounds listed in *Table I* gave normal symmetrical 'elution' peaks, with linear relationship between peak height and sample volume. When ethylene chlorohydrin was examined, however, unusual recordings were obtained, as shown in *Figure 4*, where the peak (or plateau) height was almost

constant and the length of the plateau was approximately proportional to the sample volume.

It is possible that this anomalous behaviour is due to decomposition of the chlorohydrin at constant rate. An attempt is being made to identify the decomposition products by use of a large (6 inch × $\frac{1}{2}$ inch) column fitted with a multiple cold-trapped collecting system, as described by Bradford

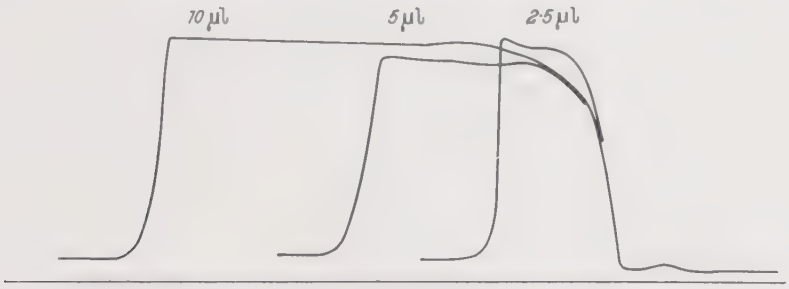

Figure 4. Ethylene chlorohydrin at 77°C *(silicone column)*

et al[3]. Ethylene chlorohydrin is the only material so far encountered which behaves in this way, and fortunately it has never been found in any of the mixtures examined.

2. Gas Analysis

Janák[8] and Ray[9] have described the analysis of hydrocarbon gas mixtures by elution from carbon at 'room' temperature whilst Patton, Lewis and Kaye[10] carried out similar separations at 180°C. In our laboratory it was found that hydrogen, methane and carbon dioxide could be estimated reasonably well by elution from carbon (Sutcliff Speakman 207 B) with nitrogen, but that the retention volume of ethane, even at 100°C, was too large to be practicable. The work of Bradford, Harvey and Chalkley[3] indicated that partition columns were as suitable for the analysis of lighter hydrocarbons as Ray had found for C_3 and C_4 gases.

The problem in hand was to determine small amounts of ethane and other impurities in ethylene and small amounts of ethylene in ethane, preferably on the same column. Hydrogen was chosen as carrier gas since the thermal conductivity cell has very low sensitivity for ethane in nitrogen. Using a 6-ft column of tri*iso*butylene at 'room' temperature Bradford *et al.* found that the separation of ethane and ethylene was insufficient to allow the determination of traces of the former in large amounts of the latter. The separation was improved by lengthening the column and lowering the operating temperature, a 20-ft tri*iso*butylene (Eastman) column maintained at 0°C in an ice bath being used. This column gave satisfactory separation at first but after a short period of use its efficiency was reduced by loss of stationary phase into the gas stream. Volatilization from the column was eliminated by saturating the carrier gas with the base liquid before use by passage through a sintered glass bubbler immersed in the ice bath. Eventually, however, it was found that equally satisfactory separations could be obtained with a 25-ft column packed with liquid paraffin.

The column is packed in stout $\frac{1}{4}$-inch polyvinyl chloride (PVC) tubing coiled in a cylindrical ice bath in the centre of which the katharometer is

mounted. Carrier gas, supplied at constant pressure, passes several times round the ice bath, through one cell of the katharometer, through the column and to atmosphere via the other thermal conductivity cell, no pumping system being used. The optimum flow rate has been found to be 22 ml/min, which requires an input pressure of 50 cm of mercury.

Calibration data for a number of gases are given in *Table II.*

Table II. Calibration Data for Various Gases

Gas	*Retention volume* ml	*Peak height per* ml *at s.t.p.* mm	*Gas*	*Retention volume* ml	*Peak height per* ml *at s.t.p.* mm
Air	185	540	*Ethane*	430	320
Methane	205	510	*Propylene*	1080	160
Carbon dioxide	290	445	*Propane*	1250	125
Ethylene	330	390	—	—	—

Air is not completely separated from methane and large amounts interfere with the estimation of this component. The long column is not suitable for analysis of mixtures containing C_4 and heavier gases since their retention volumes are too large.

Since as a rule only small samples of gas are available the by-pass pipette

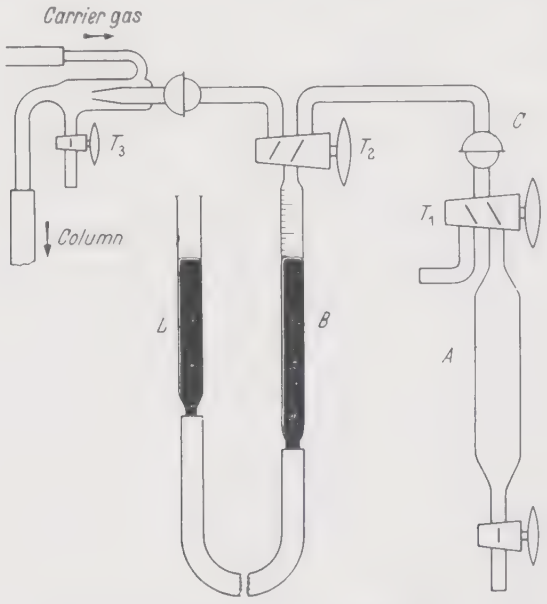

Figure 5. Gas injection apparatus. A, sample tube; B, burette, C, ball joint; L, levelling bulb; T_1, T_2, T_3, taps

system for injection has not been used, but the simple gas burette shown in *Figure 5* has proved very satisfactory. With this device as little as 2 ml of gas may be handled without contamination by air.

The special sample 'torpedo' *A* is attached by ball joint *C*, and the capillary

tube T_1-C-T_2 cleared of air by passing mercury to waste through T_1. Tap T_1 is then reversed and gas drawn into the burette B, where its volume is measured. Tap T_2 is then reversed and the sample forced on to the column by raising the levelling bulb L. The few drops of mercury which escape from the jet are withdrawn at intervals through tap T_3. For calibration with pure gases the burette B, normally of 5 ml capacity, is replaced by one of 0·7 ml capacity, whilst for preparation of mixtures of known composition the modified sample 'torpedo' shown in *Figure 6* has been useful.

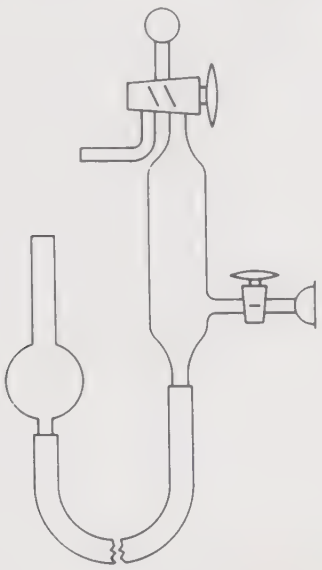

Figure 6. Gas mixing apparatus

This apparatus is filled with mercury via the levelling tube and attached to a burette similar to B in *Figure 5*. Measured volumes of various gases are introduced and mixed and the vessel is then connected to the ball joint C of *Figure 5*.

Analysis of hydrocarbon gas containing an acid gas

In addition to the normal light hydrocarbon gas mixtures a certain number of samples are received which contain up to 15 per cent v/v hydrogen chloride, in addition to methane, ethane and ethylene. Although hydrogen chloride in a gas sample may be determined readily by conventional methods it was desirable, for simplicity and speed of operation, to use the chromatographic method. It was found, however, that hydrogen chloride could not be estimated as a normal component since it was strongly adsorbed by the 'Celite' support. The difficulty was overcome by passing the sample through a 3-inch length of column, packed with finely powdered sodium bicarbonate, in front

Table III. Comparable Data on Estimation of Hydrogen Chloride

Sample No.	*1*	*2*	*3*	*4*	*5*	*6*
HCl *by chemical analysis*	11·3	12·2	15·5	9·5	1·7	6·9 % v/v
HCl *by chromatographic analysis*	11·8	12·5	15·5	9·6	1·7	7·0

of the main column. Hydrogen chloride reacts to give an equivalent amount of carbon dioxide which may be estimated by peak height measurement. Check analyses have shown satisfactory agreement between chemical and chromatographic analysis, representative data being given in *Table III*.

3. Factors Affecting the Accuracy of Chromatographic Analysis

A number of experimental variables have been studied to determine their effect on the accuracy of the chromatographic method. These factors include temperature of injection, katharometer wire temperature and katharometer block temperature.

Temperature of injection

In a recent publication Pollard and Hardy[11] discussed the effect of variation of the temperature of injection upon the separation of liquid mixtures. Our own work has confirmed their results and shows that, if peak height measurements or peak height ratios are to be used for quantitative analysis, certain precautions are necessary regarding the temperature of the 'flash heater'. For these experiments the neck of the column, just below the serum cap, was wound with a small Nichrome heater, about 1 inch long, powered by a 12 V transformer. The temperature of the column at this point was measured by insertion of a fine copper–constantan couple, the leads being taken out through the serum cap. In our apparatus the injection point was within the vapour jacket and the lowest temperature recorded was 31°C with the jacket at 35°C and 71°C with the jacket at 77°C. On the other hand the injection port of Pollard's apparatus was well away from the heating jacket and temperatures down to ambient could be used. The behaviour of *tert*butyl chloride, dichloromethane, 1:2-dichloroethane and 1:1:1-trichloroethane has been studied with a silicone column at 35°C or 77°C. In all cases nitrogen flow rate was 10 ml/min, inlet pressure 2 cm of mercury.

The variation of peak height with injection temperature is shown in *Figure 7* from which it will be seen that the magnitude of the effect differs from compound to compound. The ratio of peak heights, such as would be used in quantitative analysis with internal standards, may also vary with temperature, but the ratio of peak areas appears to be independent of temperature over the range studied (*Figure 8*). The retention volume was found to decrease with increasing temperature of injection, as shown by the values given in *Table IV*.

Table IV. Variation of Retention Volume with Temperature

Column at 35°C			*Column at* 77°C		
Temp.	*Retention volume* ml		*Temp.*	*Retention volume* ml	
	$(CH_3)_3CCl$	CH_2Cl_2		CH_3CCl_3	CH_2ClCH_2Cl
30	270	340	70	185	260
60	260	320	95	175	240
80	250	310	120	170	235
100	245	310	155	168	235

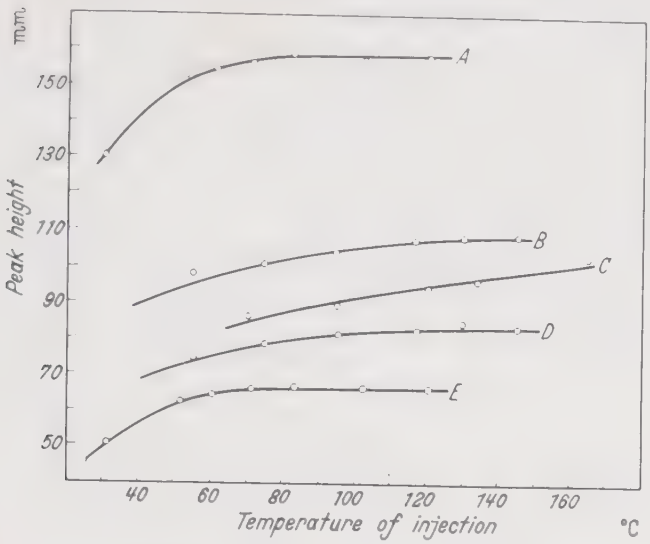

Figure 7. Effect of injection temperature

A 1 μl *Dichloromethane at* 35°C
B 2 μl 1:1:1–*Trichloroethane at* 35°C
C 1 μl 1:1:1–*Trichloroethane at* 77°C
D 2 μl 1:2–*Dichloroethane at* 35°C
E 1 μl t-*Butyl chloride at* 35°C

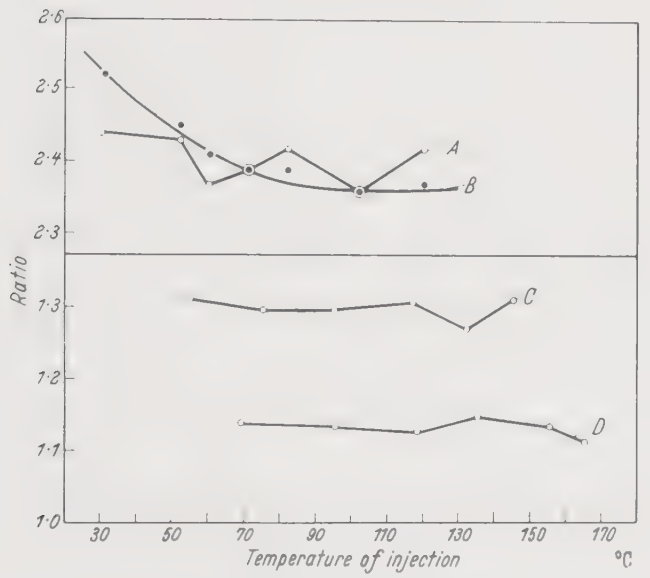

Figure 8. Ratios of peak areas and peak heights

A (*Peak area dichloromethane/peak area* t-*butyl chloride*) *at* 35°C
B (*Peak height dichloromethane/peak height* t-*butyl chloride*) *at* 35°C
C (*Peak height* 1:1:1–*trichloroethane/peak height* 1:2–*dichloroethane*) *at* 35°C
D As C, at 77°C

These results support the conclusion reached by Pollard and Hardy that, when peak heights or ratios of peak heights are used, the sample should be injected at a known temperature or at a temperature high enough to be on the flat part of the curve. Since the use of a flash heater at high temperature will affect the column operation, by heating the carrier gas, it is possible that a more logical arrangement would be to pre-heat the carrier gas to column operating temperature by passage through the vapour jacket.

Effect of katharometer wire temperature and current

The effect of the wire temperature on the sensitivity of the thermal conductivity cell has been studied by inclusion of suitable instruments in the circuit. The temperature was calculated from the cold resistance and thermal coefficient of resistivity.

Figure 9, giving peak height as a function of wire temperature, shows that there is a sharp increase in bridge output with increasing temperature, especially in the lower temperature range.

With nitrogen as carrier gas a wire current of 120 mA as at present used, gives a temperature of *ca.* 130°C (block temperature 20°C) and at this temperature 1 per cent change in current leads to 1·2 per cent change in peak height. With hydrogen as carrier gas a current of 120 mA gives a wire temperature of only 17°C (block temperature 0°C) and a change of current of 1 per cent leads to a 2·3 per cent change in peak height.

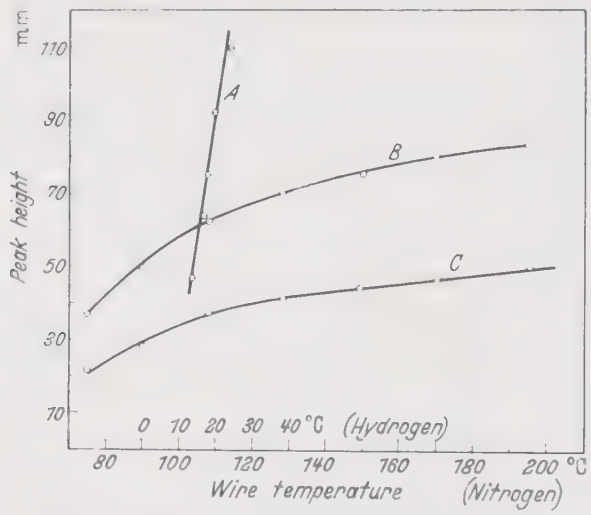

Figure 9. Effect of wire temperature on peak height

A Air in hydrogen
B 1:1–Dichloroethane in nitrogen
C 1:2–Dichloroethane in nitrogen

Since the output of the bridge network (out-of-balance p.d. due to a given change in resistance of one arm) is directly proportional to the span voltage, it was thought that higher sensitivity could be obtained by using a katharometer of higher resistance. Such a katharometer was constructed using 0·0005-inch diameter wire instead of the normal 0·001 inch. This had a cold resistance of 100 ohms, and a current of 120 mA (requiring 24 V span voltage) gave a temperature about 300°C with nitrogen as carrier gas. The sensitivity obtained was some five times that of the normal cells but the noise level was excessively high. When the current was reduced to give a reasonably stable zero, it was found that the sensitivity was but little different from that of a normal cell.

Although the sensitivity of the detector varies considerably with variation of wire current this does not seriously affect quantitative determinations when ratios of peak heights or peak areas are measured. For the analyses of gaseous samples, where the introduction of internal standards is not practicable, and

especially when using hydrogen as carrier gas, careful control of wire current is essential (see curve *A*, *Figure 9*).

Effect of katharometer block temperature

Various workers have described apparatus in which the katharometer is heated, either by means of the column vapour jacket system[1] or by a separate heater[3]. Others, e.g. Ray[1], Patton *et al.*[10], have used the thermal conductivity cell at 'room' temperature. In our laboratory the katharometer in the analytical apparatus is maintained at 30 C by means of a heater comprising a few

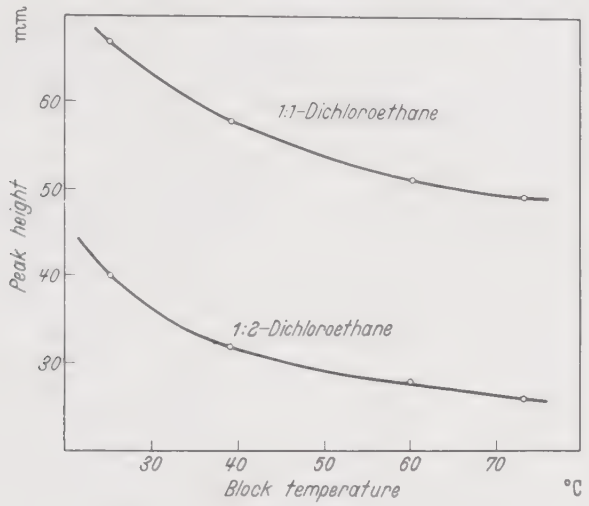

Figure 10. Effect of block temperature

turns of Nichrome wire. If this form of heater is used the current supply should be continuous, the temperature being controlled by use of a variable resistance or 'Variac', etc. A discontinuous supply, obtained by use of a contact thermometer or energy regulator, gives rise to an irregular recording, due to inductive effects on the katharometer wire. After nearly two years of operation no trouble due to condensation within the cells has been experienced. With the large (6 ft × ½ in) preparative column, where samples up to 1 ml in volume are used, it has been found necessary to heat the katharometer to about 80°C to prevent condensation of eluted fractions. That temperature control is desirable for accurate work is shown by *Figure 10* which gives the effect of block temperature on the peak height of 1:1- and 1:2-dichloroethane. A temperature variation from 25 C to 30 C results in a peak height variation of 7½ per cent for 1:2- and 6 per cent for 1:1-dichloroethane.

Note on the use of Scott's 'flame' detector

Experiments, some carried out in collaboration with Mr C. Scott of Lobitos Oilfields Co., have shown that pure hydrogen is not a suitable carrier gas for use with the heat of combustion detector[12] when methane is to be estimated. Injection of a sample, e.g. impure ethylene, on to the column results in a restriction of the flow of hydrogen, presumably due to the higher viscosity of the sample. This causes a reduction in the size of the flame and a corresponding 'negative' peak or depression on the recording. Methane emerges

from the column before the gas flow conditions have returned to normal, and appears as a minor bump at the base of the depression. Increasing the length of the column gives no improvement because, although the components take longer to emerge, the flow disturbance lasts longer. Use of a carrier gas of higher viscosity, for example, a 75–25 hydrogen–nitrogen mixture, as recommended by Scott[12], or a 70–30 mixture, largely eliminates the disturbance and allows the estimation of methane. Recordings illustrating these facts are shown in *Figure 11*.

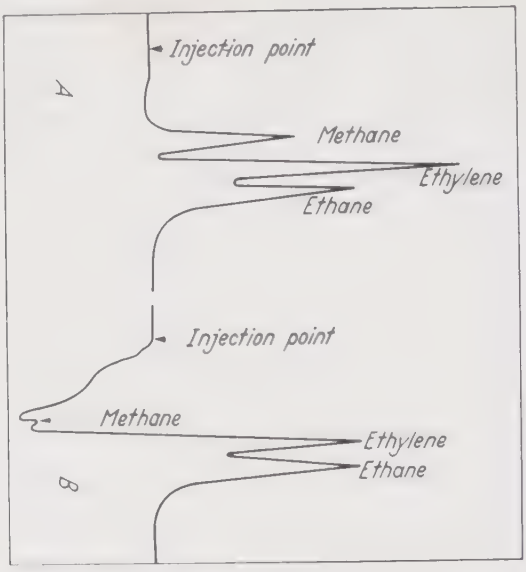

Figure 11. Results illustrating use of Scott's flame detector
A. Hydrogen 75%, nitrogen 25%. B. Pure hydrogen.
20 ft liquid paraffin column. Temperature 15°C. Flow 22 ml/min

Much of the experimental work has been carried out by Mr P. Knight and Mr M. T. Heath, and their assistance, together with that of many other colleagues, is gratefully acknowledged. Thanks are also due to Dr R. O. Gibson for his constant help and encouragement, and to the Associated Ethyl Company Limited for permission to publish this paper.

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DISCUSSION

W. A. Wiseman: Mr Harrison has described in some detail his katharometer and I should like to mention a glass cell we have found satisfactory. It has only a single wire but appears to be adequately stable and free from drift. The design is very similar to those developed by C. S. G. Phillips and has a mercury and a vapour jacket. The katharometer wire is supported from one end on copper wires brought through a B10 cone and is therefore easily replaceable.

29

THE APPLICATION OF VAPOUR PHASE CHROMATOGRAPHY TO THE EXAMINATION OF SAMPLES TAKEN FROM INTERNAL COMBUSTION ENGINES BY AN OPEN-HOLE TECHNIQUE

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Fuel quality distribution has been investigated by an 'open-hole' technique in which a small gas stream is removed from the combustion space continuously throughout the engine cycle. The techniques of vapour phase chromatography have been used to separate and analyse the extremely small samples of unburnt fuel so obtained. The method is illustrated using a 4-cylinder engine and the repeatability with which the samples may be analysed has been assessed.

Possible extension of the procedures developed to other problems in this field are discussed in the light of results obtained during this work. Since only short engine operating periods are required to obtain the samples necessary for the analysis, the use of this method is suggested for examining short term rapidly changing distribution conditions during engine acceleration.

It is well known that uneven distribution of fuel occurs in internal combustion engines fitted with a single carburettor supplying several cylinders through a divided inlet manifold system. Multiple carburettor and direct fuel injection systems have been developed to overcome this, but are too expensive for normal vehicles. The development of high efficiency engines using high octane number fuels for general purposes has made the study of maldistribution effects more important.

These effects may be divided into two types: quantity maldistribution, where the overall fuel/air ratio differs from cylinder to cylinder, and quality maldistribution, where individual components of the fuel are unequally distributed. Adequate methods of investigating quantity distribution are available, e.g. spark plug temperature measurement[1,2] and analysis of the exhaust gas from individual cylinders[3–5]. The investigation of quality distribution, is, however, more difficult, both in obtaining a representative sample of the fuel supplied to each cylinder, and in analysing the small samples available with reasonable running periods.

Although it is desirable to sample the fuel mixture being fed to each cylinder in the inlet system prior to its passage into the combustion space, it is very difficult to obtain a representative sample as, even at the inlet valve, the fuel is

not completely vaporized[6]. Most investigations of quality distribution have been carried out by examining samples taken from the combustion space by a timed valve system[7–9]. The use of electrically or mechanically operated valves, however, requires extensive modifications to the engine. In previous work moreover[6,7] the unburnt fuel vapour has been separated by condensation methods and analysed by distillation which, even when using semi-micro fractionation techniques, has necessitated fairly long running periods to obtain the amount of sample required (*ca.* a few millilitres).

A simple alternative sampling method has been developed in these laboratories, and applied by Wachal[10] to the study of the distribution of tetraethyl lead, in which a small gas stream is bled continuously from the combustion space throughout the engine cycle. This is known as the 'open-hole' technique. The open-hole gas so obtained contains a significant amount of unburnt fuel (*ca.* 1 per cent vol.) and very little partial breakdown products of a similar molecular weight to the fuel (*ca.* 1 per cent vol. of the unburnt fuel). Examination of the open-hole gas for fuel components therefore offers a possible means of investigating fuel quality distribution provided an accurate and sensitive method of analysis can be found.

The present paper describes the application of gas chromatography to this problem, the relatively small sample required for this method of analysis being especially attractive. As fuel distribution appears to be critically dependent on individual engine induction characteristics[7], this preliminary investigation has been limited to the development of suitable sampling and analytical techniques.

The investigation falls logically into two phases: the development of a suitable sampling and analytical technique using a single-cylinder engine, and the application of this method to the investigation of maldistribution effects in a 4-cylinder engine.

Equipment

Engines

The two engines employed were:

(*a*) A single-cylinder CFR engine coupled to an electric dynamometer. For most of the work an open-hole adaptor was fitted in the sparking plug hole, the plug being screwed into the detonation pickup hole.

(*b*) A $1\frac{1}{2}$-litre 4-cylinder side valve automobile engine coupled to a hydraulic dynamometer. Open-hole gas passages were drilled through the cylinder head to each combustion space (*Figure 1*).

Vapour phase chromatographic apparatus

The gas density balance apparatus described by James and Martin was employed[11,12] with an improved recording system comprising a d.c. amplifier (Leeds and Northrup type 9835B) feeding a 10 mV 1 sec potentiometric recorder (Leeds and Northrup Speedomax type G). For most of the work an operating temperature of 134 C was employed with Silicone Fluid 703 (W. Edwards and Co) as stationary phase: for some of the more volatile mixtures the apparatus was operated at 78·5 C with *n*-hexatriacontane as stationary phase. The response of the density balance is proportional to the product of the concentration of vapour in the eluant gas, and the difference in

density between the vapour and the eluant gas. The area under each peak divided by the vapour density difference between the component it represents and the eluant gas is thus proportional to the number of moles of that component present. The mole percentage composition of a mixture can therefore be calculated from area measurements made on its chromatogram. It has been found that quantitative results obtained in this way are accurate to within 1 mole per cent provided the sample can be introduced on to the column without evaporative losses. The areas were measured by cutting out the peaks on the recorder paper and weighing them. Preliminary tests showed that the paper was adequately uniform.

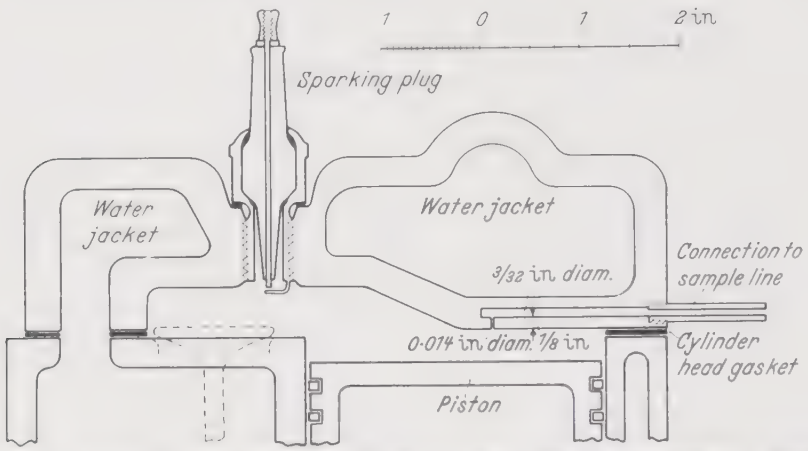

Figure 1. Section of 4-cylinder engine showing modifications for open-hole sampling

Sampling Methods

CFR engine

Initially a large volume of the open-hole gas was examined, using pure *iso*octane as fuel, in order to assess the size of sample required and to gain information on its composition. The gas stream from the engine was passed through a heated 500 ml glass sampler [*Figure 2*(a)] fitted with brass vacuum valves with polytetrafluorethylene (Teflon) diaphragms. After about 10 litres of gas had passed through from the open-hole, the valves were closed and the sampler removed from the tube furnace.

The fuel was separated by re-heating the tube and displacing the gas with nitrogen through a 'Carbosorb' trap, which removed the carbon dioxide, followed by a trap filled with calcium hydride to remove water and then into a capillary condensation trap cooled in liquid nitrogen. Some carbon monoxide condensed at first but was carried off by passing a little excess nitrogen after the sample had been swept out. A few milligrammes of frozen condensate, distinctly yellow in colour, then remained in the capillary trap. This was examined by connecting the trap to the top of the chromatograph column, warming it gently until the sample evaporated and displacing the vapour on to the column with the eluant gas, nitrogen. Although the sample was much too large the condensate appeared to consist almost entirely of the fuel, *iso*octane. An interesting pattern of partial breakdown products amounting to about 1 per cent of the condensate was, however, apparent (*Figure 3*); this will be discussed later.

Further experiments showed that about 5 ml of open-hole gas contains sufficient fuel vapour to give an adequate peak for the fuel hydrocarbon, operating the density balance detector of the chromatographic apparatus at

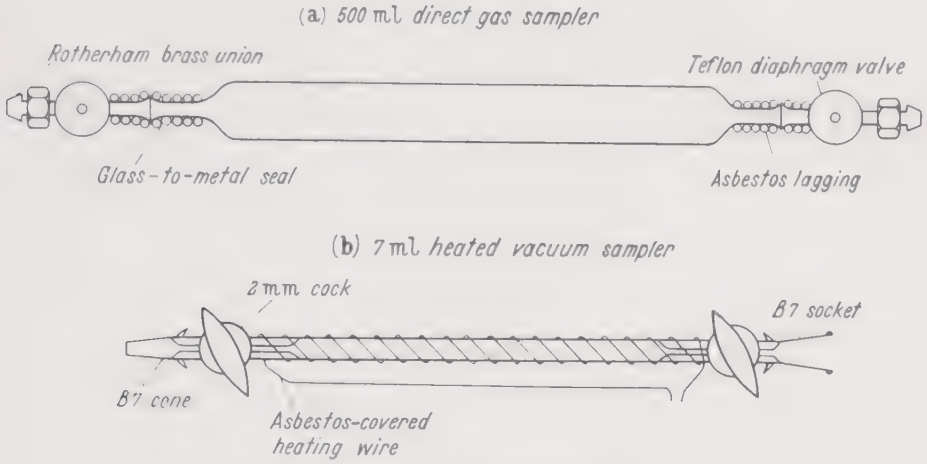

Figure 2. Gas sampling tubes

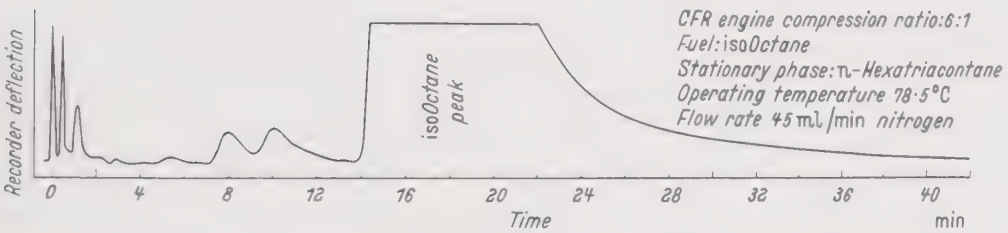

Figure 3. Chromatogram showing partial breakdown products from isooctane, 500 ml *direct sample*

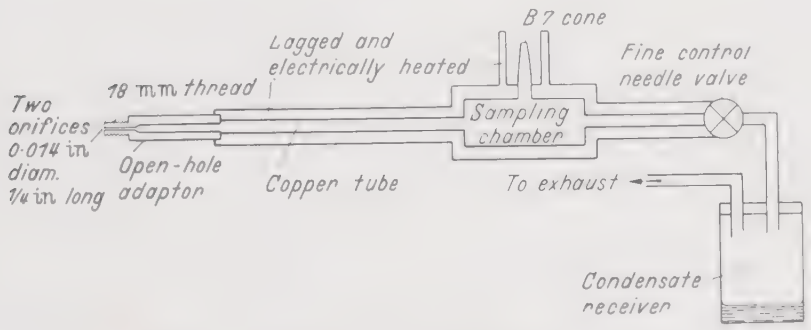

Figure 4. CFR engine by-pass sampling apparatus

maximum sensitivity. With this very small volume requirement it is possible to collect the sample in an evacuated receiver [*Figure 2*(b)] and pass the gas from the heated receiver into the chromatographic apparatus through a calcium hydride water trap without prior separation by condensation.

Typical results with a *n*-hexatriacontane column using this method for a binary fuel of approximately equal proportions of *iso*octane and methyl*cyclo*hexane are given in *Table I*. It was found more convenient to install a

Table I. Results of Direct Examination of Small Open-hole Gas Samples from the CFR Engine

Test	*Fuel analysis* mole per cent	
	iso*Octane*	*Methyl*cyclo*hexane*
Fuel, as blended	44·8	55·2
Fuel from carburettor, as tested	44·0	56·0
Open-hole sample 1	42·7	57·3
Open-hole sample 2	44·1	55·9

Column: *n*-hexatriacontane at 78·5°C

heated copper tube leading from the sampling adaptor on the engine and to remove the gas samples from a small reservoir inserted in the tube (*Figure 4*). It was then only necessary to heat the sample container above the dew point of the gas before displacing the sample into the column with the eluant gas. The effect of the position of the sampling point in the combustion space was investigated by interchanging the sparking plug and open-hole adaptor. In the detonation pickup hole the adaptor was situated partially inside a pocket in one corner of the combustion space, but in spite of this apparently poorly scavenged position, no significant differences either in the proportion or composition of the unburnt fuel in the gas were observed.

The usefulness of this method of sampling was limited with components of high volatility by the large peak for hydrogen which was formed in the calcium hydride trap. This difficulty can be overcome by using hydrogen instead of nitrogen as eluant gas with some small loss of sensitivity of the density balance. With components boiling above 120° C the peak height/peak width ratio becomes too low to allow accurate measurement of peak area. A stationary phase giving shorter retention times than *n*-hexatriacontane gives some improvement in this respect, though it is of course accompanied by some loss in resolution for high volatility components. Silicone Fluid 703 was employed, giving about half the retention volumes of *n*-hexatriacontane: a hydrocarbon boiling at 200° C appears after about half an hour operating at 134° C with a flow rate of 50 ml/min. However, where the fuel contains several components boiling above 120° C, this direct examination of the open-hole gas becomes less effective as the large sample required reduces the resolution achieved in the chromatographic analysis. For this reason a new sampling method was sought.

The retention volumes of volatile materials in partition columns vary markedly with temperature. It is thus possible to employ a short partition

column at relatively low temperature as a vapour trap, provided that the sample volume passed does not exceed the break-through volume for the most volatile component it is desired to include in the analysis.

A new sampling technique was developed in which a portion of the open-hole gas was passed through a short partition trap at room temperature (*ca.* 2 inches long with Silicone Fluid 703 as stationary phase, *Figure 5*).

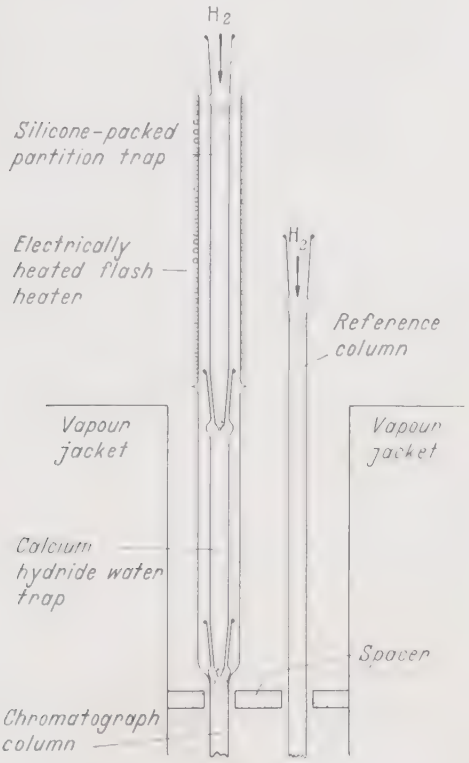

Figure 5. Modified chromatographic head for use with partition and water traps

This trap could then be detached, temporarily closed by glass caps and transferred to the chromatographic apparatus, where the vapours could be eluted into the column in the usual way after the trap had been brought to the column operating temperature.

A heated sample line from the open-hole adaptor similar to that used for direct gas sampling was employed, except that an adjustable needle valve was fitted in the sample exhaust to control the flow rate through the trap (*Figure 4*) which retained only the fuel hydrocarbons, partial breakdown products, and most of the water. To exclude the water from the chromatograph column, various dehydrating agents were tried, including calcium and barium oxides, phosphorus pentoxide and calcium hydride. Calcium hydride appeared to be the most satisfactory, in that it had a very low adsorption for the hydrocarbon vapours. The fact that it yields hydrogen on reaction with water made it necessary to use this gas as eluant. The calcium hydride trap was at first placed before the partition trap on the engine, but later it was found more convenient to fit it inside the vapour jacket of the chromatographic apparatus

as shown in *Figure 5*, thus simplifying the sampling arrangements on the engine.

Before employing the method on the multi-cylinder engine it was necessary to assess the accuracy with which the composition of the fuel supplied to the cylinder could be determined by analysis of the open-hole gas, even when components differed widely in volatility. The following precautions were taken to achieve the best results:

1. To economize in test fuel it was necessary to use it only for a short period prior to sampling. Previous runs have shown that some contamination of the test fuel persisted for at least fifteen minutes after changing over from the warm-up fuel, even with careful flushing of the fuel feed system. Any errors due to this were eliminated by using a pure hydrocarbon as warm-up fuel, which could be resolved from the test fuel components in the chromatographic analysis.

2. As the partition trap is only attached to the heated sample take-off tube during sampling, it had been found that some condensation occurred in the cool dead-space between the conical joint and the packing. This end of the partition trap was therefore preheated in a separate small tube furnace prior to sampling to ensure that the sample deposited only in the column packing, where evaporative loss in the subsequent handling would be least.

3. To check that none of the sample had passed through the partition trap, a second trap was connected in series and its contents examined separately. By measuring the volume of open-hole gas passed through the trap with a soap-film flowmeter, the maximum permissible sample volume for any particular type of trap and fuel could be determined.

A series of tests was carried out with the CFR engine using a binary fuel, *iso*octane and decalin, which had been blended gravimetrically. For the purpose of these tests the two stereo-isomers of decalin (which boil about 8C° apart) present in the commercial hydrocarbon employed, although resolved in the analysis, were considered together. The results are given in *Table II*,

Table II. Results of CFR Engine Test using Partition Trap Procedure

Fuel	*Fuel analysis* wt per cent		
	iso*Octane*	*Decalin*	*Confidence limits for 95% probability*
Gravimetric blend	40	60	
Open-hole fuel sample	41	59	±2%

and it may be seen that the mean result of the open-hole gas analysis agrees to within 1 mole per cent of the blended composition.

Four-cylinder engine

Previous work[7] with multi-cylinder engines has shown that individual engine induction characteristics are probably more important than fuel volatility in determining the distribution pattern. Therefore no attempt has been made to carry out a detailed study of distribution effects in this particular engine, but

merely to illustrate how the partition trap procedure already described may be employed for this purpose.

The work has been confined to the boiling range in which maldistribution effects due to volatility differences would be most significant, i.e. approximately 100–200 C. The binary fuels shown in *Table III*, which all had

Table III. Fuels used for Distribution Tests

Fuel	*Component*	*B. pt* °C 760 mm Hg	*Composition* wt %
A	iso*Octane*	99	44·5
	Ethylbenzene	136	55·5
B	iso*Octane*	99	58·9
	Cumene	152	41·1
C	iso*Octane*	99	40·1
	Decalin	—	59·9
Decalin	trans*Decalin*	187	64·2
	cis*Decalin*	195	35·8

*iso*octane as one component, were employed. Commercial decalin was used in fuel C. During the course of the work it became apparent that the *cis* and *trans* isomers were being distributed differently and they were therefore considered separately. The composition of the commercial hydrocarbon was obtained by a prior chromatographic determination.

The open-hole gas passages in the cylinder head are shown in *Figure 1* and the sampling apparatus for one cylinder in *Figure 6*. Each open-hole orifice was 0·014 inch in diameter and $\frac{1}{8}$ inch long. Each heated sampling tube, fitted with a fine control valve and sample take-off tube, was joined to a cylinder head connection by a short length of silicone rubber tubing. The partition traps were connected by standard cone and socket joints (B7) and short lengths of silicone tubing to the sample take-off tubes. The valves and all connections were heated by electric windings. Thermocouples were fitted to check sampling line and engine temperatures. A short tube heater was fitted over each sampling outlet, to heat the sample take-off tube, the silicone tube, the B7 joint and the trap up to the start of the partition packing. Two soap-film flowmeters were mounted above the sampling apparatus with flexible connections together with a set of four preheaters for the partition traps. A shield was fitted to screen the sampling apparatus from the engine fan draught.

After warming up the engine using an appropriate hydrocarbon, usually toluene, the fuel supply was disconnected and when the engine stopped it was restarted using the test fuel. This procedure was repeated to ensure satisfactory flushing of the fuel system. After 3 minutes a set of partition traps complete with end caps was placed in the preheaters. Two minutes later the traps were transferred to the sample take-off tubes, after removing the caps

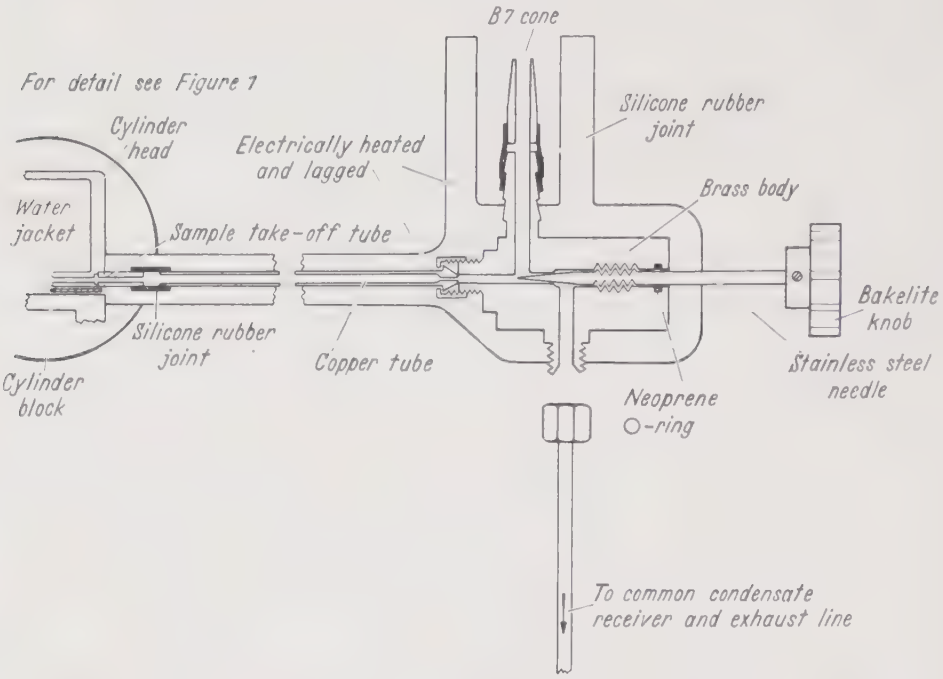

Figure 6. Diagrammatic layout of one sampling line on the 4-cylinder engine

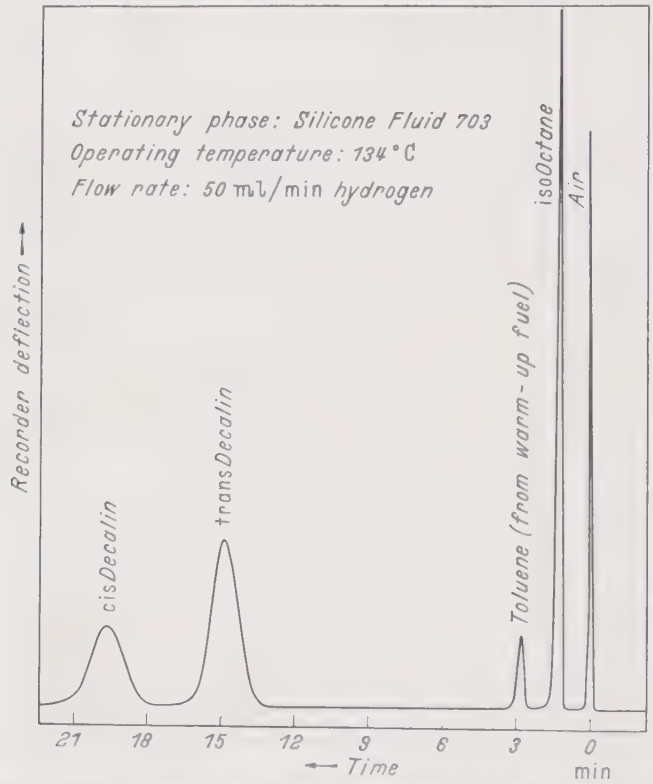

Figure 7. Typical chromatogram of isooctane/decalin fuel 'C' taken as open-hole sample from the 4-cylinder engine

and connecting the soap-film flowmeters. The rate of sample flow was regulated by the adjustable needle valves, and when the required sample volume, as measured by the flowmeters, had passed the traps were disconnected and the caps replaced.

The contents of the tubes were analysed chromatographically by connecting them to the top of the column fitted with a calcium hydride trap (*Figure 5*). After heating them in the small tube furnace to the column operating temperature the sample was eluted with hydrogen.

A typical chromatogram obtained with Fuel C is shown in *Figure 7*. The three peaks in each due to the fuel components may be seen, together with a small peak for the warm-up fuel, toluene. Quantitative analyses were carried out by cutting out the peaks corresponding to the test fuel components from the recorder paper and weighing them as described earlier. The results obtained are shown in *Table IV* and diagrammatically in *Figure 8*.

Table IV. Results of Distribution Test using Fuel C

Component	*Cylinder number*	*Fuel analysis:* wt per cent			*Distribution coefficient R*
		Decalin isomer	iso*Octane*	*Confidence limits for 95% probability*	
trans*Decalin*	*1*	43·9	56·1	±2·0	0·78
	2	46·7	53·3	±2·6	0·87
	3	56·7	43·3	±2·7	1·31
	4	51·1	48·9	±3·1	1·04
	Original fuel	50·1	49·9	—	—
cis*Decalin*	*1*	29·9	70·1	±2·6	0·76
	2	32·0	68·0	±2·2	0·84
	3	43·4	56·6	±2·3	1·36
	4	37·0	63·0	±3·9	1·04
	Original fuel	36·0	64·0	—	—

Test fuel composition: 40·1% *iso*octane, 38·4% *trans*decalin, 21·5% *cis*decalin

Mean fuel analysis from all four cylinders: 39·0% *iso*octane, 39·1% *trans*decalin, 21·9% *cis*decalin

A similar pattern was found with the other fuels, but in order to simplify the presentation of the data the results are given in terms of a distribution coefficient for each cylinder. This coefficient R is a measure of the change in

proportion of any given fuel component relative to some standard component due to maldistribution effects and is defined as:

$$R_n = r_0/r_f$$

where r_0 = mass ratio of the given fuel component to the standard component in the open-hole gas, r_f = mass ratio of the given fuel component to the standard component in the test fuel, and n = cylinder number.

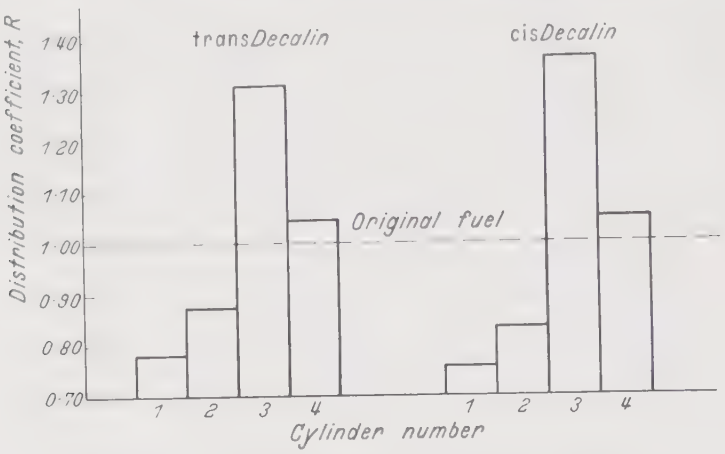

Figure 8. Distribution diagram for decalin isomers

The standard component throughout was *iso*octane. The collected results are given in *Table V* and are plotted in *Figure 9*. They show serious maldistribution within the boiling range of normal gasoline, the effect increasing with the boiling point of the component concerned.

Table V. Summary of Distribution Tests

Component	*B. pt* C	*Distribution coefficient*			
		R_1	R_2	R_3	R_4
iso*Octane*	99	1·00	1·00	1·00	1·00
Ethylbenzene	136	0·96	0·94	1·07	1·03
Cumene	152	0·89	0·93	1·12	1·03
trans*Decalin*	187	0·78	0·87	1·31	1·04
cis*Decalin*	195	0·76	0·84	1·36	1·04

Other Applications

The method developed has interesting possibilities for investigating the combustion processes which occur in the engine. The fact that the open-hole gas is issuing from the combustion space during the entire engine cycle, and that little reaction can occur after it has passed the open-hole, suggests that it

should contain a fairly representative selection of stable intermediates in the oxidation reaction chain. Some preliminary experiments were carried out by passing the open-hole gas for about fifteen minutes through a trap cooled in liquid nitrogen. The trap was then removed, and allowed to warm up slowly

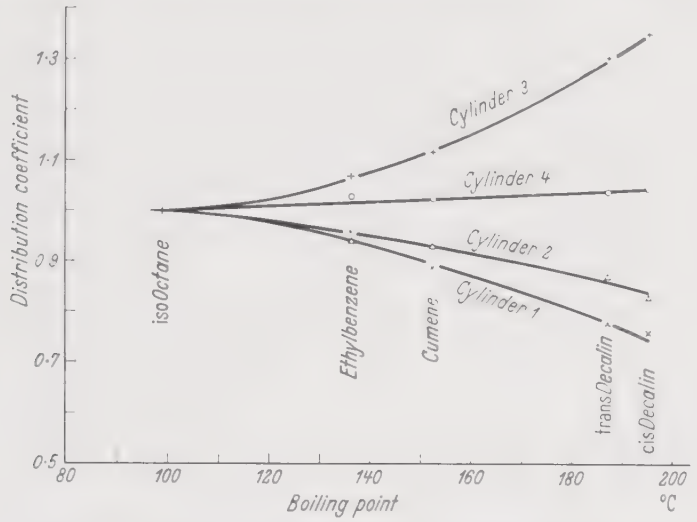

Figure 9. Quality distribution curves for the 4-cylinder engine

until finally a few drops of liquid with a larger quantity of water remained. This was centrifuged and the hydrocarbon layer separated and dried. A 50 microlitre sample was separated chromatographically on an *n*-hexatriacontane column operating at 78·5°C. The chromatograms in *Figure 10*

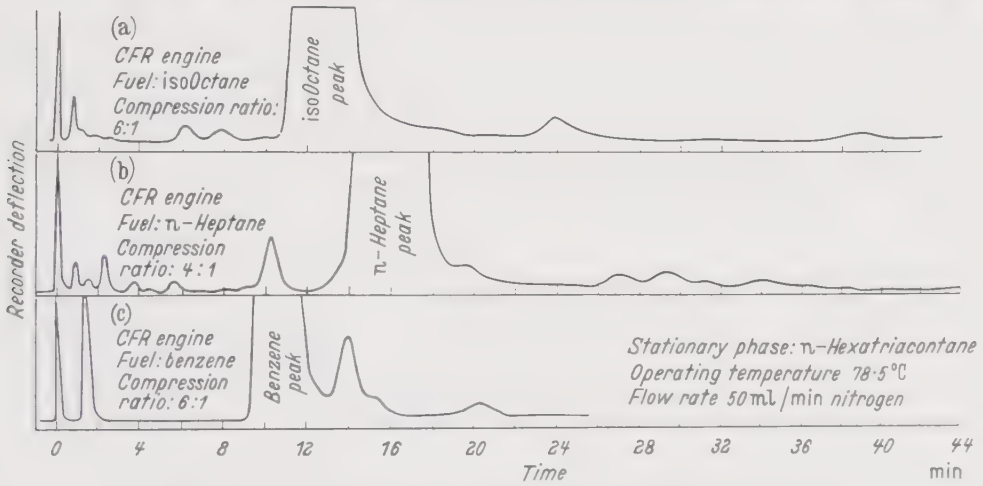

Figure 10. Chromatogram showing partial breakdown products, using pure hydrocarbons as fuels

show the results obtained with three separate hydrocarbons as fuel: *iso*-octane, *n*-heptane and benzene. Little information has so far been obtained on the structure of the partial breakdown or oxidation products shown in these chromatograms, but the fact that the general pattern is so markedly different is significant.

By isolating a larger sample of the condensibles from the open-hole gas it should be possible to carry out a preliminary type separation and analyse the resulting fractions chromatographically using appropriate stationary phases. A similar technique would be of value in investigating the higher boiling trace components in exhaust gases.

Conclusions

The application of the techniques of vapour phase chromatography has overcome many of the difficulties associated with the problems of concentrating and collecting the fuel vapour from the open-hole gas stream. Furthermore the small size of sample required, together with the speed with which the analysis may be carried out, promises to extend the scope of quality distribution studies to short term rapidly changing engine conditions. For example, under accelerating conditions from slow speed, maldistribution effects probably become even more pronounced than during constant speed running[8]. The versatility of the types of separation which can be achieved, together with the high sensitivity and separation efficiency which may be obtained with vapour phase chromatography, make the methods described very attractive for the investigation of the combustion reactions which occur in an engine.

The authors thank the Chairman of the British Petroleum Company Limited for permission to publish this paper.

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DISCUSSION

A. I. M. Keulemans: In the first place, I should like to congratulate the authors on the way in which they found a very elegant application of this technique. I think we are about at the stage when this technique is opening up new fields in quite a few branches of research, and I think this is the first example that shows the importance of the tool in technical respects. Thank you very much.

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CHEMICAL ENGINEERING DESIGN OF A UNIT FOR CONTINUOUS GAS CHROMATOGRAPHY (HYPERSORPTION)

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In connection with separation of the end gas of partial oxidation of methane, the one-pass recovery of acetylene on activated carbon by continuous gas chromatography was investigated. After a short description of the technique and of the pilot unit, investigations concerning the dimensioning of the adsorption and rectification sections of the chromatograph column, as well as calculation methods are reviewed. The calculations are controlled by measurements made in the pilot unit. In this unit, an acetylene-free top product, and acetylene as bottoms product of a purity above 98 per cent have been produced, and important parameters of the process elucidated. Finally, principles for the chemical engineering design of the continuous chromatographic column are given, on the basis of which a unit on commercial scale was designed.

Various methods for the production of acetylene, based on the partial oxidation of natural gas, have recently been developed all over the world. In these processes the composition of the gaseous mixture obtained in the oxidation reactor is, after quenching and cooling, approximately the following: 8–9 per cent acetylene, 4–5 per cent carbon dioxide, the same quantity of methane, 25 per cent carbon monoxide, and more than 50 per cent hydrogen. Different techniques are employed for the recovery of acetylene, such as scrubbing with water under pressure, multi-stage selective solvent absorption, and combined adsorption–absorption processes. In the latter method, acetylene and carbon dioxide are first separated from the accompanying gases by continuous adsorption (hypersorption). According to data taken from the literature, this gas contains besides carbon dioxide a maximum quantity of 82·8 per cent by volume of acetylene, and is further purified by absorption rectification to recover acetylene of a purity of above 98 per cent[1].

This conception is confirmed by *Figure 1*, showing the adsorption isotherms on activated carbon of the gases listed above[2]. It can be gathered from the figure that the isotherms of acetylene and carbon dioxide exhibit considerably greater adsorption values than those of the other components, and it would therefore seem obvious to remove these two gases by adsorption. The closely similar run of the isotherm of carbon dioxide and that of acetylene shows, however, that the separation of these components is not practicable by simple adsorption. After extensive theoretical and experimental study of the continuous gas chromatography process it has been stated that there are no theoretical or practical obstacles to the direct production of pure acetylene

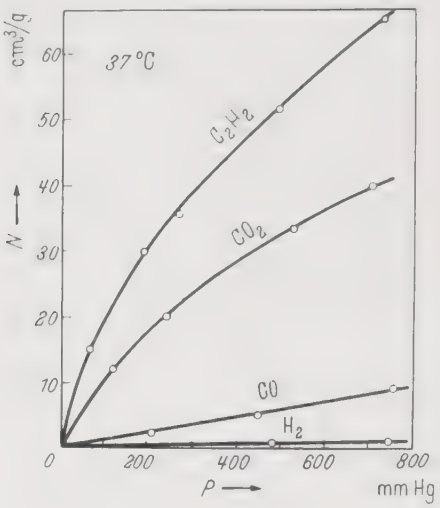

Figure 1. Isotherms of C_2H_2, CO_2, CO and H_2 on activated carbon
(*Courtesy of* Industrial and Engineering Chemistry *and the Phillips Petroleum Company*)

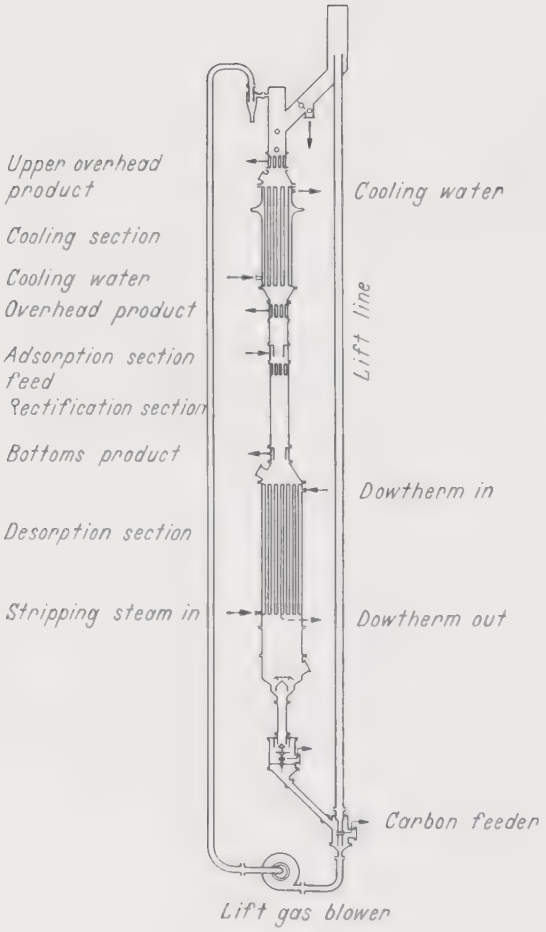

Figure 2. Schematic diagram of pilot plant

from the end gases of partial oxidation. As a result of this, the second, absorption, step of the combined process may be eliminated, and the resolution of the partial oxidation gaseous mixture can be effected in a three-product hypersorber, wherein acetylene is produced as bottoms product, carbon dioxide as a side-cut, and the remaining components, which may be considered inert as far as adsorption is concerned, are obtained as overhead product.

Should the synthesis gas obtained as overhead product serve the purpose of ammonia production, whereby carbon monoxide is converted and carbon dioxide separated from the gaseous mixture by scrubbing, the employment of a two-product hypersorption unit is more economical, as in this process acetylene is obtained without production losses and free of carbon dioxide as bottoms product, and the total quantity of carbon dioxide emerges overhead. Such a system is schematically represented[3] in *Figure 2*.

Description of the Unit

The chromatograph column consists of four sections. The upper section is a shell and tube heat exchanger, providing for cooling the hot activated carbon, delivered to the top of the column by gas lift. The second section is the adsorber, the third one constitutes the rectification section proper, whereas the fourth section, a shell and tube heat exchanger, is the so-called desorber. The column is packed along its total length by activated carbon, which moves downwards owing to its own weight at a given velocity, and is then delivered to the top by gas lift. Regulation of the velocity is carried out without the employment of a moving carbon feeder by means of setting, or regulating, the injector of the lift feeder. A definite quantity of activated carbon is therefore in constant circulation in the chromatographic unit.

Outstanding features of the pilot plant examined are given as under.

The diameter of the chromatograph column in the adsorption and rectification sections is 25 cm and 20 cm respectively; the effective height of the column is approximately 26 m. The total height of the adsorber and of the rectification section, i.e. that of the separation section proper, is 5 m. The length of the shell and tube cooler is 3·5 m, and of the desorber, 4·5 m. Both comprise 1 inch tubes. Activated carbon passes downwards in the tubes. The experiments were carried out at 1·5 atm pressure on average. The quantity of the gas feed was 28–30 m^3 (s.t.p.)/h. The feed gas contained 7 per cent acetylene and 4 per cent carbon dioxide. Operating at a carbon velocity of 200–220 kg/h, the overhead product contained at most traces of acetylene, and the bottoms product was acetylene of a purity above 99 per cent.

The gaseous mixture to be resolved is fed to the bottom of the adsorption section. The gas passes countercurrent to the activated carbon moving downwards and is disengaged at the top of the adsorption section. Beside the acetylene, part of the carbon dioxide is adsorbed in the adsorption section, the adsorption isotherms of the two gases having a closely similar run. By passing downwards, the activated carbon with the adsorbed gases reaches the rectification section. Sharp separation is brought about by the exchange between the adsorbed phase passing downwards on the moving carbon, and the desorbed phase, i.e. the acetylene reflux, recycled countercurrent to the activated carbon; the acetylene is enriched on the activated carbon due to its greater adsorbability, so that the carbon passing from the rectification

section to the desorber finally contains pure acetylene in adsorbed state. This is released due to both the high temperature (280 C) prevailing in the desorber, and the injection of steam (0·7 kg steam/kg acetylene). Part of the desorbed gas is withdrawn at the top of the desorber as bottoms product, while the rest is returned as a reflux to the rectification section. There is an upwards pressure drop in the column, which means that a one-way gas flow prevails all along it.

Realization of the process outlined together with the chemical engineering design of the chromatograph column required extensive investigations. Only the questions arising as to the adsorption and rectification sections will be dealt with in detail.

Adsorption from Gas Streams—The Working Zone

If a mixture consisting of acetylene and an inert gas is passed through a fixed bed of activated carbon, after a given length of time from the commencement of the experiment the acetylene emerges in the carrier gas leaving the activated carbon bed. The concentration of acetylene increases and finally reaches the acetylene concentration in the feed gas. The experimental results are presented in *Figure 3*, where break-through times taken on activated carbon columns of

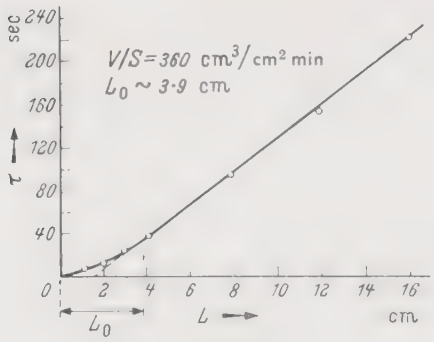

Figure 3. Break-through time under dynamic adsorption conditions as function of carbon height

different heights are plotted as a function of zone length. It can be gathered from *Figure 3*, that above a given zone height the correlation becomes linear, which means that the advancing velocity of the concentration distribution section, i.e. of the so-called working zone, is constant and the length of the working zone remains unchanged. Using *Figure 3*, the length of the working zone can be estimated; this represents the length over which the above-mentioned linear correlation holds good. The advancing velocity of the working zone can also be determined from this figure. The correlation between the break-through time and the zone height being linear, the length of the working zone will not be changed during its advance. If the working zone advances during a given length of time, τ, as far as L cm, this means that during the same time a zone of L cm length is saturated with acetylene. The adsorption capacity of the activated carbon is known from the adsorption isotherm of acetylene. Assuming that the adsorption process takes place from flowing gas streams under isothermal conditions, estimation of the advance of the working zone presents no difficulties[4].

If a gaseous mixture, the concentration of which is C_0 (cm³ acetylene per cm³ total mixture), is introduced at a velocity of V cm³/min into an adsorbent layer with a cross section of S cm² and the working zone has advanced L cm during τ minutes, the charged acetylene quantity during the same length of time ($C_0V\tau$) is equal to the quantity of adsorbed acetylene (aSL), assuming the acetylene content of the gas filling the free space of the carbon bed may be neglected. In the present investigation this represents an error below 1 per cent. Therefore

$$C_0V\tau = aSL \qquad \ldots.(1)$$

where a (cm³ acetylene/cm³ adsorbent) denotes the equilibrium static activity of the adsorbent at an equilibrium concentration C_0. The advancing velocity of the working zone from equation (1) will be

$$u = L/\tau = C_0V/aS \qquad \ldots.(2)$$

The justification of the calculation method described is given in *Table I*. A mixture of 9·3 per cent acetylene and of 90·7 per cent hydrogen was passed

Table I

V/S cm³/cm² min	$u_{calc.}$ cm/min	$u_{meas.}=L/\tau$ cm/min	L_0 cm
174·5	1·86	1·92	2·7
270·0	2·87	3·10	3·6
600·0	6·38	6·95	5·2

through a column of activated carbon at different velocities. The experimental and calculated values of the advancing velocity of the working zone are in satisfactory agreement in the experiments at different velocities. The equilibrium static activity of acetylene is taken from *Figure 4*, showing the

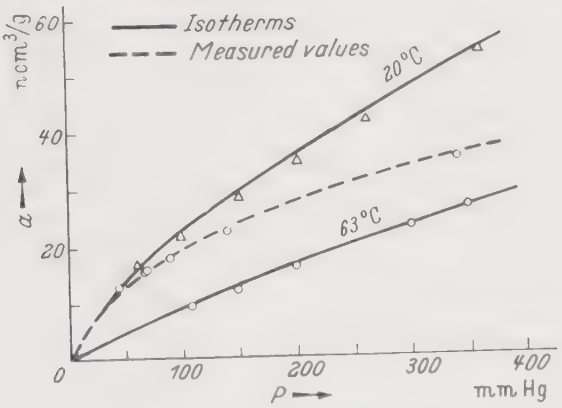

Figure 4. Isotherms of C_2H_2 on activated carbon 'Nuxit A'

isotherms of acetylene on the activated carbon employed in these investigations, determined by conventional method[5]. The equilibrium static activity of the acetylene, a, amounts to 17·5 cm³ (s.t.p.) per gramme = 8·75 cm³ (s.t.p.) per cm³.

The differences between calculated and measured values may be explained as follows. If break-through experiments on activated carbon beds of different heights can be carried out under isothermal conditions, the equilibrium static capacity at a given acetylene concentration may be calculated from the measured advancing velocity of the working zone (L/τ), and a point of the isotherm of acetylene is obtained. According to equation (2)

$$a = \tau C_0 V/LS \qquad \ldots.(3)$$

The 'isotherm plots' of acetylene for gaseous mixtures of various concentrations at a temperature of 20° C have been taken by this method, and are presented in *Figure 4*. It can be gathered from this that the deviation between the two curves increases with increasing partial pressure of acetylene. This may be due to the fact that during the dynamic experiments no time is available to remove the heat of adsorption, as a result of which the temperature of both the activated carbon and the gas rises. Another consequence is that under dynamic conditions the adsorbent cannot be saturated up to the equilibrium static activity, and this explains the deviations between the calculated and measured a values shown in *Figure 4*. Each point of the dynamic 'isotherm', calculated from the advancing velocity of the working zone, belongs to different isotherms. The ratio of the calculated and measured values of the advancing velocity of the working zone thus represents the degree of saturation of the activated carbon.

Dimensioning of a Continuous Adsorber

On dimensioning the continuous adsorber, two important points must be taken into account, viz.

(*1*) The total quantity of gas to be recovered (acetylene) should be adsorbed without losses

(*2*) The gas adsorption capacity of the adsorber should be utilized to the greatest possible extent.

The acetylene quantity fed to the adsorber in unit time is C_0V.

The gas adsorption capacity of the adsorbent passing through the adsorber in unit time is $a_d Sw$, where w denotes the linear velocity of the activated carbon, and a_d denotes the dynamic activity.

These two assumptions hold good if

$$C_0 V = a_d S w \qquad \ldots.(4)$$

From this, the velocity of the moving carbon

$$w = C_0 V/a_d S \qquad \ldots.(5)$$

From equations (2), (3) and (5) it follows that

$$w = u_{\text{meas.}}$$

The velocity of the carbon bed must therefore be set to equal the advancing velocity of the working zone.

The above relationship is valid only when the height of the activated carbon bed above the gas feed point is greater than, or equal to, the length of the working zone ($L \geq L_0$). If this is so, the working zone in the adsorber is formed along the length of L_0, calculated from the feed point, and does not

advance. If the carbon velocity in the adsorber becomes greater, that is when $w > u$, then

$$C_0 V < a_d S w \qquad \ldots.(6)$$

and

$$C_0 V/Sw < a_d \qquad \ldots.(7)$$

which means that the acetylene quantity adsorbed by unit volume of activated carbon is smaller than the equilibrium activity. Due to this, the activity of the carbon is not used to the full, and an excess quantity is circulated in the system.

On the contrary, if $w < u$, then

$$C_0 V/Sw > a_d \qquad \ldots.(8)$$

and the acetylene quantity adsorbed by unit volume of carbon is larger than the equilibrium activity, as a result of which the working zone advances in the adsorber at a given velocity and after the length of time of $(L-L_0)/(u-w)$ has elapsed, it will break through even an adsorbent zone of the length L.

As a consequence, the dimensioning of the continuous adsorber must be carried out to meet these two requirements:

(*1*) The carbon velocity should equal the advancing velocity of the gas front ($w = u$), and

(*2*) The height of the adsorption zone should be greater than the length of the working zone ($L > L_0$).

The correlations given for the dimensioning of the continuous adsorber have been controlled in a laboratory hypersorber with a diameter of 1 inch, employing a gaseous mixture of acetylene and nitrogen containing 7–8 per cent acetylene. The dimensioning of the pilot unit was carried out on the basis of these findings. The deviations between the values calculated from the batch experiments and those measured in the experiments with moving bed were within 10 per cent. The height of the adsorber in the pilot plant was considerably oversized in order to compensate with ease for the fluctuations due to an increase in the gas flow or to changes in acetylene concentration, without allowing acetylene to be released to the overhead gas.

The method detailed above may be applied for the case also when there are two components to be adsorbed from the carrier gas instead of one, such as acetylene and carbon dioxide[6]. In such cases there are two working zones in the adsorption section, and the advancing velocities of these are different. The advancing velocity of the working zone for the component with lower adsorbability, in our case for carbon dioxide, is smaller than that for acetylene. For the purpose of acetylene recovery, only the adsorption of acetylene must be taken into account in dimensioning the adsorber. For mixture adsorption, however, the components mutually lower each other's adsorbability, which means that in the presence of carbon dioxide, smaller quantities of acetylene are adsorbed than from pure acetylene. From a practical standpoint, it is therefore necessary to determine the length and the advancing velocity of the working zone for acetylene only, in the presence of carbon dioxide of a given concentration.

Another point must also be taken into consideration when dimensioning the adsorber of the chromatograph column, namely that not only the acetylene and carbon dioxide content of the feed gas must be accounted for

in connection with distribution conditions formed in the adsorber, but also the carbon dioxide and acetylene quantities reaching the adsorption section from the rectification section, which also influence the development of the adsorption process. According to this, any dimensioning of the adsorber, taking into account only the composition of the feed gas, will give only approximate values; precise dimensioning can only be carried out with a knowledge of the separation process, i.e. of the functioning of the rectification section.

Rectification of a Mixture of Pure Carbon Dioxide and Acetylene—Reflux Ratio

If the rectification section of the hypersorber is filled up with the mixture of acetylene and carbon dioxide without moving the activated carbon, the gas samples taken at various heights of the rectification section will have identical composition. If the carbon flow is started without further feeding or withdrawal of product, the acetylene and carbon dioxide transported into the desorber in the adsorbed phase will be desorbed due to the higher temperatures prevailing there and to the presence of steam, and an upward gas flow will result. From the flowing gas the acetylene, having greater adsorbability than that of carbon dioxide, is retained in larger quantities, and displaces the carbon dioxide to a certain extent from the adsorbed phase; the latter is enriched at the top of the rectification section and is adsorbed on fresh carbon delivered there[7].

After the lapse of a certain length of time, concentration differences develop along the rectification section (see *Figure 5*, $a'b'c'd'$), and finally

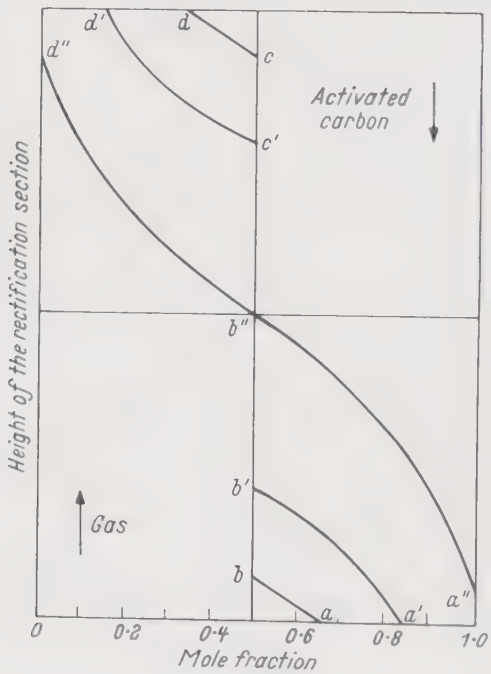

Figure 5. Concentration distribution of mixture C_2H_2–CO_2 on activated carbon

steady state conditions will be reached ($a''b''c''d''$). It can be seen in the figure that, in a column of adequate length, there is only pure acetylene at the bottom of the column up to a certain height, whereas pure carbon dioxide can be found at the top. This means that the working rectification zone falls between dead zones, which do not participate in the rectification process, and the length of which does not influence the length of the working rectification zone. There being neither feeding nor withdrawal of products in the rectification section, it is justified to assume that the rectification is carried out at total reflux.

Rectification may be performed also by withdrawing the same quantities of carbon dioxide and acetylene from the top and bottom of the column respectively, as have been introduced into the system. It is obvious that the feed point of the carbon dioxide–acetylene gaseous mixture without carrier gas should be at that part of the rectification section where the composition of the gas phase is identical with that of the gaseous mixture to be fed. According to the fact that under these circumstances total reflux is no longer employed, the working zone of the rectification section is somewhat changed.

The acetylene quantities [a' cm^3(s.t.p.)/gramme] adsorbed on the activated carbon leaving the rectification section are disengaged in the desorber. Part of the desorbed acetylene [equivalent to the acetylene feed quantities, n^0 cm^3(s.t.p.)/h] is taken as a product, while the rest is returned to the rectification section as a reflux. The ratio of the acetylene quantities returned as a reflux to those withdrawn as bottoms product is called reflux ratio. If a^0 denotes the equilibrium adsorption capacity belonging to the partial pressure of acetylene in the feed gas, taking into consideration the circumstances of mixture adsorption, the minimum mass velocity ($W_{\text{min.}}$ g/h) of the carbon will be

$$W_{\text{min.}} = n^0/a^0 \qquad \ldots.(9)$$

and the minimum reflux ratio

$$R_{\text{min.}} = \frac{W_{\text{min.}}a^t - W_{\text{min.}}a^0}{W_{\text{min.}}a^0} = \frac{a^t - a^0}{a^0} \qquad \ldots.(10)$$

The conception of the minimum reflux differs here from that used in distillation calculations. The equation shows that there exists a possibility of increasing the reflux ratio by increasing carbon velocity. This, however, means that the adsorption capacity of the carbon is not made use of, which increases the costs of carbon transportation and those due to attrition losses. It is therefore best to carry out rectification under, or near, minimum reflux conditions.

On the basis of the above discussion it is evident that an analogy exists between the distillation and continuous chromatography of binary mixtures. This analogy provides for the development of a 'plate-to-plate' calculation method for the dimensioning of the technological process schematically shown in *Figure 2*. In order to effect this calculation, the experimental study of the adsorption of binary mixtures becomes necessary.

Adsorption of Acetylene—Carbon Dioxide Mixtures

Important investigations have recently been carried out on mixture adsorption by Lewis and co-workers[8], as well as by Bering and Serpinskii[9]. Lewis and

co-workers have studied the equilibrium relations of hydrocarbon mixtures on activated carbon and silica gel, and have published equilibrium curves for over 30 binary gaseous mixtures. They have also examined the effects of gas composition, temperature, and pressure on adsorption equilibria. To denote the selectivity of adsorption, they employ the following expression, the meaning of which is identical with the relative volatility, α, well known from distillation calculations:

$$\alpha = \frac{x_a y_b}{y_a x_b} = \frac{N_a y_b}{N_b y_a} \qquad \ldots.(11)$$

where x = mole fraction in the adsorbed phase, y = mole fraction in the gas phase, N_a and N_b = number of moles adsorbed from the mixture/gramme of adsorbent, a index refers to acetylene, and b index refers to carbon dioxide. In adsorption calculations, α is usually termed the separation factor or

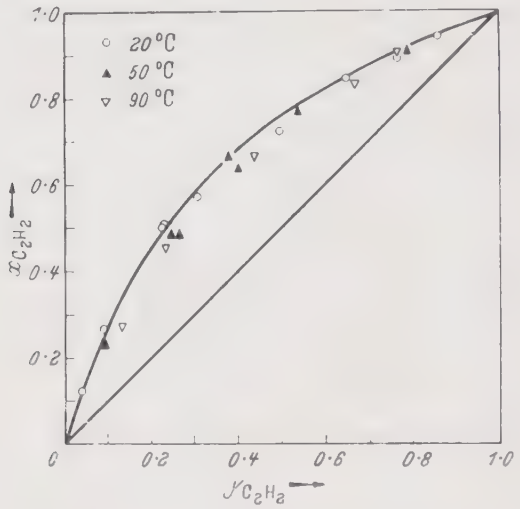

Figure 6. Equilibrium curve C_2H_2–CO_2 *on activated carbon 'Nuxit A'*

selectivity coefficient. According to experimental data, the separation factor α is practically independent of gas composition at constant total pressure, and slightly decreases with a rise in pressure. Nothing has been communicated as to the effect of temperature for lack of sufficient experimental data.

In the course of investigations covering the quantitative relations of mixture adsorption, it has been found that the relationship between the total adsorbed quantity and the composition of the equilibrium gas phase is non-linear. The experimental data obtained are described by the following equation where

$$\frac{N_a}{N_a^0} + \frac{N_b}{N_b^0} = 1 \qquad \ldots.(12)$$

N_a^0 and N_b^0 denote the amounts adsorbed of the pure components at the total pressure of the mixture (mole/gramme).

In order to prove the validity of equations (11) and (12), the adsorption equilibria of the acetylene–carbon dioxide mixtures were investigated on activated carbon in laboratory equipment. Measurements were carried out in the apparatus described by Lewis *et al.*[10], which was slightly modified by us.

The data obtained for the isothermal isobaric adsorption of acetylene–carbon dioxide mixtures at 20°C are summarized in *Table II*. Similar measurements were carried out at 50 and at 90°C also.

Table II

Adsorption of Acetylene–Carbon Dioxide Mixture on Activated Carbon 'Nuxit A' at 20°C and atmospheric pressures (736–745 mm Hg abs.)

Adsorbed C_2H_2 cm^3/g	*Adsorbed* CO_2 cm^3/g	*Total adsorbate* cm^3/g	C_2H_2 mole *fract. in gas phase* $y_{C_2H_2}$	C_2H_2 mole *fract. in ads. phase* $x_{C_2H_2}$	*Separation factor* α
64·3	3·77	68·07	0·853	0·945	2·95
59·2	7·08	66·28	0·762	0·892	2·58
55·2	9·97	65·17	0·647	0·847	3·03
45·7	17·04	62·74	0·496	0·728	2·72
34·4	25·35	59·75	0·308	0·576	3·00
29·2	27·82	57·02	0·236	0·512	3·40
29·1	28·35	57·45	0·227	0·506	3·49
14·2	38·45	52·65	0·091	0·269	3·67
6·02	44·2	50·22	0·041	0·120	3·19

Mean value of $\alpha = 3{\cdot}11$

The equilibrium curve from the phase composition data summarized in *Table II* is presented in *Figure 6*. The last column of the table shows α values according to equation (11). On the basis of experimental data, the value of α is practically independent of gas composition, which is in good agreement with the experimental results of Lewis and co-workers, as well as with those of Bering and Serpinskiĭ. The maximum deviation from the mean value (3·11) is 16 per cent, while the average deviation amounts to *ca.* 10 per cent.

This agreement seems to be fair considering the accuracy of liquid–vapour equilibrium measurements generally. It should be mentioned that among the α values calculated by us from the data of the very precise mixed adsorption experiments of Bering and Serpinskiĭ, more than 20 per cent deviation from the mean could also be found. The equilibrium values taken at 50 and 90 C are also given in *Figure 6*. Hardly any data have been published covering the correlation of the separation factor and temperature. According to most of the investigators, the separation factor is independent of temperature; some of them, however, state that it slightly decreases with increasing temperature. The mean value of our measurement data at various temperatures appears to confirm that the value of α decreases somewhat with temperature rise.

Figure 7 illustrates quantities of adsorbed acetylene, carbon dioxide, and total amount of adsorbate as a function of the acetylene mole fraction in the equilibrium gas phase, on the basis of the data given in *Table II*. The two limiting values represent the adsorbed quantities of the pure components at a total pressure of the mixture ($P = P_{C_2H_2} + P_{CO_2}$). (The value of P is less than atmospheric pressure, due to the enrichment of inert contaminants in the

acetylene and carbon dioxide). This plot is similar to the x/P diagrams employed with vapour–liquid equilibria investigations.

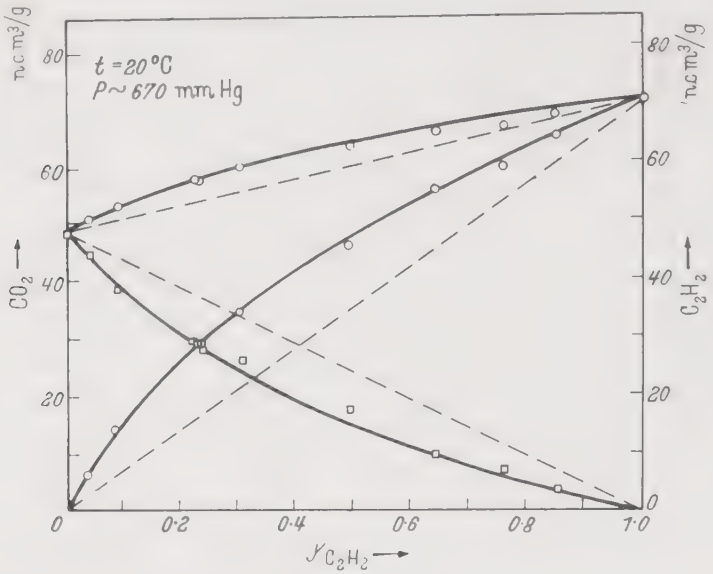

Figure 7. Plots of mixture adsorption correlations as functions of gas phase composition

In adsorption of gaseous mixtures, the amounts adsorbed of each component are lowered; that of the component with higher adsorbability decreases slightly, whereas that of the other component is considerably reduced. The total amount adsorbed is between the adsorbed quantities of the two components in the pure state. If the separation factor α is equal to

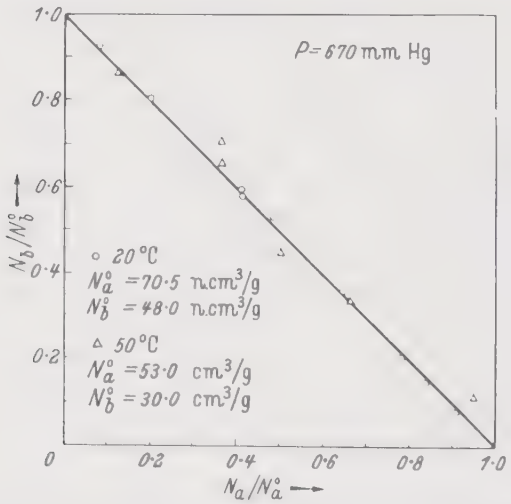

Figure 8. Plots of mixture adsorption measurements based on equation (12)

the ratio of the quantities adsorbed from the two pure components, i.e. $N_1^0/N_2^0 = \alpha$, the adsorbed volumes of the individual components are directly

proportional to the mole fractions of the individual components in the gas phase, and the total adsorbed volume is a linear function of the gas phase composition. The plots in *Figure 7* correspond to the case when $\alpha > N_a^0/N_b^0$ and $N_a^0 > N_b^0$.

Experimental data were also revised on the basis of the empirical equation published by Lewis and co-workers. In coordinates (N_a/N_a^0), (N_b/N_b^0) the experimental data are represented by a straight line, cutting both axes at unit length. The above plot is shown in *Figure 8*. It can be seen in the figure that the experimental data form a straight line with fair approximation, and that the average deviation amounts to *ca.* ± 5 per cent.

As the justification to apply relations (11) and (12) to the adsorption of acetylene–carbon dioxide mixtures has thus been proved experimentally, the equations of the partial isotherms of the components can also be derived. Introducing the terms $y_A = y$, and $y_B = 1 - y$, the partial isotherm equations of acetylene and carbon dioxide will be

$$N_a = \frac{N_a^0 N_b^0 \alpha y}{N_b^0 \alpha y + N_a^0 (1 - y)} \qquad \ldots\ldots(13)$$

and

$$N_b = \frac{N_a^0 N_b^0 (1 - y)}{N_b^0 \alpha y + N_a^0 (1 - y)} \qquad \ldots\ldots(14)$$

respectively. The total quantity of adsorbed gas

$$A = N_a + N_b = \frac{N_a^0 N_b^0 (\alpha y + 1 - y)}{N_b^0 \alpha y + N_a^0 (1 - y)} \qquad \ldots\ldots(15)$$

Applying the equation of the equilibrium curve, the total adsorbed quantity can be expressed as a function of the acetylene mole fraction in the adsorbed phase

$$A = \frac{N_a^0 N_b^0}{N_b^0 x + N_a^0 (1 - x)} \qquad \ldots\ldots(16)$$

where x denotes the mole fraction of the acetylene in the adsorbed phase, and $1 - x$ that of carbon dioxide.

Calculation of the Rectification Section

The analogy between the sorption process taking place in the rectification section and the distillation process means that the calculation and dimensioning of the rectification section is similar to that of packed towers. The determination of the height of the rectification section thus involves the calculation of the number of theoretical plates, and of the height equivalent to a theoretical plate (HETP). An important deviation from conventional distillation calculation methods arises from the fact that the mole numbers of the gas and of the adsorbate, respectively, passing at various tower heights are different, and the assumption of a constant molal flow, which would considerably simplify calculations, cannot be made. This is connected with the fact that the gas adsorption capacity of the activated carbon constantly varies due to the change of gas composition on the one hand, and that of the temperature

on the other hand, and in the course of the stepwise calculation the material and heat balance must be determined individually for each transfer unit.

The rectification section is calculated 'plate-to-plate'. The plates are numbered upwards, beginning at the desorber. According to prevailing temperature and pressure, there is respectively on the first plate A_1 cm^3/g gas and A_1x_1 cm^3/g acetylene in adsorbed state, which is totally disengaged in the desorber. Part of the desorbed gas is the product (T), while the rest is returned as reflux to the rectification section (G_0). The acetylene concentration in the product gas amounts to the required y_T value, therefore $x_1 = y_T$.

Owing to the above, the total and partial material balance on plate No. 1 will be as follows:

$$A_1 + G_1 = A_2 + G_0 \qquad \ldots.(17)$$

$$A_1x_1 + G_1y_1 = A_2x_2 + G_0y_T \qquad \ldots.(18)$$

from which

$$A_1 - G_0 - A_2 - G_1 = T \qquad \ldots.(19)$$

$$A_1x_1 - G_0y_T = A_2x_2 - G_1y_1 = Ty_T \qquad \ldots.(20)$$

The value of A_1 may be calculated from equation (16). Upon selection of the reflux ratio

$$T = A_1/(R + 1) \qquad \ldots.(21)$$

The value of G_0 can be taken from equation (19).

According to the assumptions, the gas flowing upwards from the theoretical plate No. 1 is in equilibrium with the adsorbed phase passing downwards. Once x_1 is known, y_1 can be expressed from the equilibrium relation [see equation (11)].

In the material balance, G_1, A_2 and x_2 are unknown quantities. However, only two equations are available, namely equations (19) and (20). The third equation necessary for the solution of the problem can be obtained by expressing A_2 as a function of x_2 and substituting it into the two equations mentioned.

$$A_2 = \frac{N_a^0 N_b^0}{N_b^0 x_2 + N_a^0(1 - x_2)} \qquad \ldots.(22)$$

From equation (19)

$$G_1 = A_2 - T$$

Substituting the values of G_1 and A_2 into equation (20), we have

$$\frac{N_a^0 N_b^0}{N_b^0 x_2 + N_a^0(1 - x_2)} \cdot x_2 - \frac{N_a^0 N_b^0}{N_b^0 x_2 + N_a^0(1 - x_2)} \cdot y_1 + Ty_1 = Ty_T \qquad \ldots.(23$$

Upon rearrangement and reduction, we get for x_2 the following expression

$$x_2 = \frac{N_b^0 y_1 + T(y_T - y_1)}{N_b^0 + T(y_T - y_1)(1 - N_b^0/N_a^0)} \qquad \ldots.(24)$$

Figure 9(a) shows the acetylene content of the gas phase as a function of the number of theoretical plates, based on the 'plate-to-plate' calculation. In *Figure 9*(b), the acetylene content of the gas phase is plotted as a function of the height of the rectification section, in accordance with measurement data

taken in our pilot unit. Both figures contain three curves, which correspond in pairs to approximately identical reflux rates. In our theoretical calculations, the dead-zone ($y_T = 0{\cdot}98$) at the bottom of the rectification section was not taken into account, and the starting points of the curves are therefore at identical heights. During the experiments, however, a dead-zone was formed at the bottom of the rectification section, at different heights in each of the

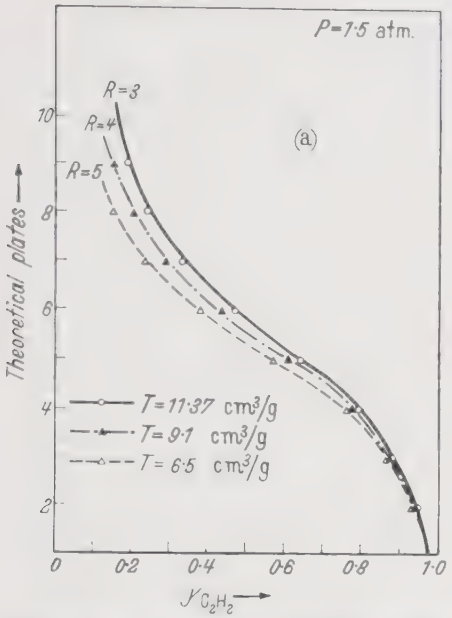

Figure 9(a). *Calculated concentration distribution of rectification section*

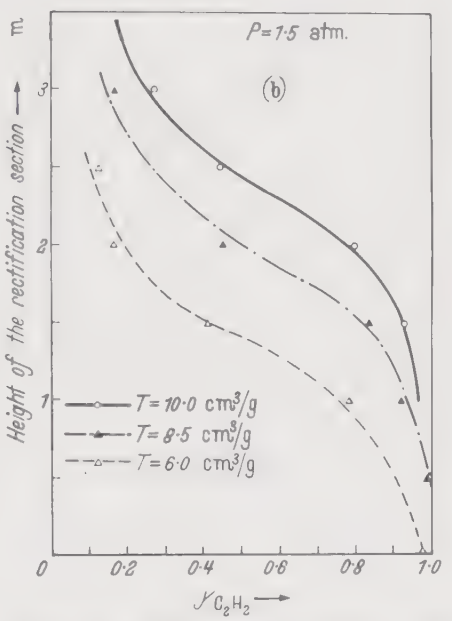

Figure 9(b). *Concentration distribution measured in rectification section of pilot unit*

three cases, which resulted in a relative displacement of the starting points of the curves. The dead-zone is necessary for the smooth working of the system in order that fluctuations connected with the feed should not influence the purity of the bottoms product. The closely parallel run of the curves obtained from gas analytical data, and those from calculation is obvious enough.

The determination of the height of the rectification section is carried out by employing the calculated number of theoretical plates and the experimentally established height equivalent to a theoretical plate (HETP). In this pilot plant, the height equivalent to a theoretical plate was determined for different reflux ratios. As shown in *Figure 9*(b), the value of this is 30 cm, to fair approximation. In the pilot unit, the minimum rectification section height to achieve the desired separation amounted to 2·5–3 m.

Establishment of the feed point is carried out on the basis of the concentration distribution curve; this differs to some extent from the conventional method employed in distillation calculations. If we want to withdraw the carbon dioxide with relatively high adsorbability at the top of the adsorption section together with the overhead gas, the acetylene–carbon dioxide mixture flowing upwards from the rectification section will charge the activated carbon in the adsorption section. It is therefore desirable to reduce the acetylene content of the gas flowing to the adsorption section to a minimum in order to

avoid as far as possible charging of the activated carbon. Correct dimensioning will be based on the material and energy balance calculations of the adsorption section.

Principles of the Chemical Engineering Design

The above section has dealt with our investigations and calculation methods concerning the adsorption and rectification sections of the continuous gas chromatograph column. The first step to the chemical engineering design of the chromatographic unit is the calculation of the material balance of the system. With the knowledge of the gas through-put in each section, the calculations covering the adsorption and rectification sections may be effected according to the above principles. These calculations can be carried out by employing the adsorption isotherms, the dynamic adsorption data, the values of differential heats of adsorption, and the separation factors determined at various temperatures.

With the knowledge of the operation of the separation section and of the carbon velocity, the heat balance of the chromatograph column can be determined, and on the basis of this, the dimensioning of the heat exchangers can be settled. This method is identical with the heat transfer calculations applied to reactors with moving beds. This method of calculation gives correct results for the dimensioning of the desorber also, the heat transfer velocity being considerably smaller than that of the desorption, and it is therefore not necessary to consider desorption kinetics. For dimensioning the heat exchanger, knowledge of the specific heat of the activated carbon, of the heat transfer coefficient values (which vary with carbon velocity), as well as of that of the cooling water and Dowtherm requirements is necessary.

The diameter of the column and the internal cross sections of the individual sections are determined from the carbon and gas velocity data, taking into account prevailing flow conditions.

To accomplish the separation of gases, it is of first importance to avoid mixing of the gaseous systems formed in the chromatograph column. The correct direction of gas flow can be ensured by suitably adjusting the prevailing pressures, and by constructional elements of precise dimensions, inserted between the individual sections; these are so-called hydraulic locks, providing for considerable pressure drop. It is of prime importance to prevent mixing of the lift system gas and of pure acetylene released in the desorber, i.e. there should be no gas flow at the bottom of the column in either direction. As a consequence of this, the gas lift system dimensioning should meet the requirement that the pressure drop of the system be identical with the pressure drop developed in the chromatograph column under normal operating conditions. Another important requirement for the dimensioning of the gas lift system is to reduce to a minimum the attrition losses of the activated carbon during transportation. With a knowledge of the chromatograph column dimensions and knowing the gas through-put, the pressure drop in the individual sections of the column, resulting from the gas flow, may be calculated. With a view to unidirectional flow, the pressure drop values can be added up. For pressure drop calculations, the relation published by Ergun[12] was used; calculated results were in good agreement with measurement data from pilot plant experiments. Dimensioning of the

auxiliaries of the chromatograph column (gas systems, heat exchangers, cyclones, etc.) presented no particular difficulties.

By means of the reviewed calculation methods and technical considerations, on the basis of measurements made in our 1 inch laboratory equipment, we constructed a pilot unit with a capacity of 30-35 m^3 (s.t.p.)/h. The experiences with, and measurements made in, this pilot unit enabled us to design a plant capable of processing partial oxidation end gas streams at a daily capacity of 90,000 m^3 (s.t.p.).

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DISCUSSION

A. Klinkenberg: The word chromatography should only be used for absorption, adsorption, extraction or ion exchange *in percolators*, i.e. with one phase stationary as contrasted to the countercurrent mode of executing the same processes.

The process discussed by Freund *et al.* thus is the countercurrent analogue of gas-solid adsorption chromatography. In gas solid adsorption chromatography the solid has a dual role, viz. as the adsorbent and as the support. Thus in the countercurrent analogue we must move the solid in view of its being the adsorbent.

In the countercurrent analogue of gas-liquid partition chromatography, however, the solid can be omitted altogether, i.e. this becomes extractive distillation.

W. A. Wiseman: I am afraid I am not very familiar with extractive distillation techniques, but I have always thought that the distillation process depends on pressure and that had a considerable effect on the temperature at which it could be carried out. Vapour phase chromatography is, however, as far as I can make out, completely independent of pressure.

N. H. Ray: May I be allowed to say a word in this discussion myself in answer to Dr Klinkenberg? While it is undoubtedly true that the large-scale equivalent of liquid gas partition chromatography is extractive distillation, one of the most important features of Dr Martin's technique (if I may so call it) is the extremely high efficiency which you can obtain in a short length of this packing, which cannot possibly be achieved in the kind of packing over which a liquid may be run. It has occurred to me that one might, for example, pack a column with Raschig rings and flow liquid down it with an uprising gas stream, but clearly this would not achieve anything like the order of separation that can be obtained on a finely divided solid packing. As far as the movement of the solid, or liquid, or the effect of which you

move and which you keep stationary on the name of the process is concerned, I feel myself that it does not really matter whether it is stationary or moving, in view of the fact that you can always consider motion of this type as being purely relative.

A. KLINKENBERG: I think that once you get the solid in a column moving and make a countercurrent process of it, the height equivalent to the theoretical plate will increase above the value to which we are accustomed in chromatography.

E. GLUECKAUF: I should like to refer to the point which the Chairman has just raised, namely the theoretical plate height which can be achieved in a situation where a liquid runs countercurrent to a gas. It is quite clearly not as good as that which can be obtained in the chromatograph column. However, theoretical plate heights of 5 mm are quite attainable, and one can achieve very effective separation in this way.

W. A. WISEMAN: I do not think it is necessary to use a solid support. I do not see any reason why it should not be feasible to have a liquid fall down the column in a spray. That is one possibility. Alternatively there is no reason why you should not have the column filled with liquid up which the gas can pass in fine bubbles. The principal difficulty is getting uniform size of bubbles and I am unable to suggest how this might be done.

D. AMBROSE: I think that what Mr Wiseman has just been describing is in fact an example of the usual countercurrent process of the chemical engineer. In connection with the comparison of extractive distillation with chromatography I would just like to mention some experiments which have only just been begun. I have found that in a column containing dry Celite it is quite possible to allow water to percolate down against a countercurrent flow of air. From a usual distillation point of view one would imagine such a column would flood immediately. In fact if the feed on to the column packing is done by capillary action with filter paper, and it is then withdrawn, again by capillary action, so as to prevent the formation of slugs of liquid, it is quite possible to persuade the solvent to run down countercurrent to an upward flow of gas. The idea of this came as an extension of using the chromatograph column, though I do not suggest it could be extended to a large scale. If it could be used then it would be precisely analogous to an extractive distillation column.

31

VAPOUR FRACTOMETRY (GAS CHROMATOGRAPHY), PART II A POWERFUL NEW TOOL IN CHEMICAL ANALYSIS

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The Perkin–Elmer Corporation, U.S.A.

Because of analytical versatility never before encountered in low-cost instrumentation, vapour phase chromatography has recently become an accepted new tool in routine chemical analysis and research. In spite of the simplicity of the method, earlier acceptance has been somewhat delayed because of insufficient emphasis on partition methods in the chromatography of gases.

Vapour phase chromatography is competing to a certain extent with already established methods such as mass, Raman, infrared and ultraviolet spectroscopy or recording fractional distillation. In order to clarify the position of vapour phase chromatography equipment in the field of analytical instrumentation, a comparison with the previously mentioned techniques is presented.

Quantitative methods and sampling devices are also discussed, since these represent a major factor in determining the future success and popularity of vapour phase chromatography in industrial and research laboratories.

WHEN observing the rapid growth and development of the technique of vapour phase chromatography (VPC), analysts and instrument manufacturers often arrive at the question: 'What present methods does this new technique replace and what is the actual position of VPC equipment in the line of existing analytical instruments?'

Essentially VPC lends itself to analytical problems that have usually been submitted to investigations by mass-, i.r.-, u.v.- and Raman-spectroscopy or recording fractional distillation techniques. Most of these require expensive instrumentation and qualified technical personnel. Therefore the field of analytical chemistry is very anxious to determine the extent to which this new method, attractive in simplicity and cost, will compete with these established methods.

In comparison with mass spectrometry VPC has the advantage of providing increased resolution or separation of components, since it permits easy separation of isomers. However, the method at this stage only allows for investigating molecules up to approximately 200–300 in molecular weight with boiling points up to 250–300 C, thus being inferior to the present mass spectrometer range. Substances having very low boiling points such as some inorganic compounds cannot yet be separated satisfactorily and require special modifications of standard VPC equipment such as refrigeration and

unusual column length. Another serious limitation arises from the spread of the boiling range of various components in a mixture. In general the best compromise between resolution and speed of operation is obtained when using operating temperatures corresponding to the lowest boiling substance present in the sample mixture. When operating at 50°C for example, components of boiling points not more than *ca.* 130C° can still be eluted in a reasonable time. At operating temperatures of 150C° the last components running through at tolerable speeds will have boiling points of 230°C or so. On the other hand if temperatures higher than the boiling points of components are used, serious losses in resolution or separation efficiency will result. Thus one becomes limited to mixtures of which the components have boiling points not more than 80–100C° apart. Mass spectrometry, however, permits investigation of samples with components which cover a greater boiling range. Still, the simplicity of calculations and cost of VPC equipment make it considerably more attractive for those problems which can be handled by both methods.

In comparison with i.r.-, Raman- and u.v.-spectroscopy the advantage of VPC resides again in simplicity, lower cost, absence of interference between components, easy calculations and greater sensitivity in trace analysis. However, from a qualitative point of view, the method has much less to offer since it provides no direct molecular or structural information. Furthermore, spectroscopic techniques have none of the boiling point or range limitations and can be applied to analytical work with solids and high molecular weight materials without difficulty.

In comparison with recording fractional distillation techniques VPC has a superior separating efficiency since the chromatographic method provides a factor of 50–100 more in theoretical plates and is also considerably faster. One disadvantage, however, is the fact that crude samples have to be separated in advance from solids and high molecular weight components, since these would ultimately clog operating columns and equipment. Fractional distillation also provides possibilities for lump analysis and is generally operated in such a manner, where only components of interest are measured, the rest being grouped under one total amount for residues, total hydrocarbons above a certain carbon number, volatile fractions, etc. This is not possible in VPC since complete quantitative data are only obtained in measuring peaks of all components present.

One other major contribution of VPC to chemical analysis will eventually result from the very promising aspects of trace analysis.

It has been shown that a simple detector such as a thermal conductivity cell provides surprisingly high sensitivity for components appearing at the exit of the column. For instance, normal pentane will give a full recorder scale deflection for one milligramme of pentane injected into the stream of carrier gas at practically zero noise level. The sensitivity decreases reciprocally to retention time for slower moving components since band width is gained at the sacrifice of peak height for higher boiling substances. For the determination of a trace component, additional sensitivity can be obtained, if required, by increasing the amount of sample introduced into the system. The signal per unit percentage concentration thus increases at the same rate without decreasing stability of the instrument. Therefore the resulting signal-to-noise

ratio is increased at no loss or squeeze of other instrument performance. This has always been a weakness of the spectroscopic techniques.

The only limitations in trace analysis, by increasing the total sample amount, result from the fact that the major component band may broaden to such an extent that it will start to interfere with the trace component, and that for extremely large samples trapezoidal band shapes will be encountered.

Therefore the place of VPC in analytical instrumentation can be summarized as follows:

(*1*) To a certain extent VPC competes with the previously mentioned techniques. In such cases the competition is very strong in view of the relatively great simplicity and low cost of the equipment.

(*2*) For analytical applications in industry and research VPC represents a versatile equipment which every laboratory should have and could afford.

(*3*) In the line of analytical instrumentation it is a complementary tool (like every new method of instrumentation) which will probably provide new possibilities in trace analysis, separations and new approaches in routine quantitative analysis or process control.

Since the popularity of VPC depends entirely on its potentialities in routine quantitative analysis, it is essential that suitable techniques and equipment be developed to permit high accuracy in sample transfer and measurement.

The following quantitative methods are in use:

(a) *Internal standard technique*

This consists of accurately adding a known amount of arbitrary compound (internal standard) to the sample mixture. Calibration curves can then be established by taking ratios of peaks at varying concentrations of components to the peak of the internal standard. This provides straight line plots. (Peak heights are linear with concentration when symmetrical band shapes are obtained. They are found to be generally as accurate as peak areas.) In this manner, the peak height of the internal standard is the actual measure of total mixture inserted into the stream of the instrument if this total volume cannot be determined very accurately by the syringe method. The choice of such an internal standard depends entirely on the nature of the components to be determined and also on the concentration range in which these are present. It is generally recommended that the internal standard peak should be located in close proximity to the peaks of the components to be determined without overlapping, and that its range of concentration be chosen to produce peak heights similar to the components of interest. In this manner, reproducibility of measurement will be quite satisfactory even if running conditions such as flow rate and temperature have varied slightly from run to run.

(b) *Internal normalization*

Assuming a constant signal in the detector for each component, the area under each peak represents a direct measure of mole percentage concentration since thermal conductivity is linear with number of molecules present. The signal in the detector, however, is proportional to the difference in thermal conductivities between carrier gas and component. Average components have thermal conductivities which will vary between 0·4 and 0·6 as compared

to air. Therefore, with nitrogen as carrier gas, errors up to 30 per cent will be introduced unless corrections are made for thermal conductivity. Unfortunately, available tables are very limited in compounds for doing this. However, quite satisfactory corrections can be made by assuming that the thermal conductivity of a molecule is inversely proportional to molecular weight or gravity. If helium or hydrogen is used as carrier gas (thermal

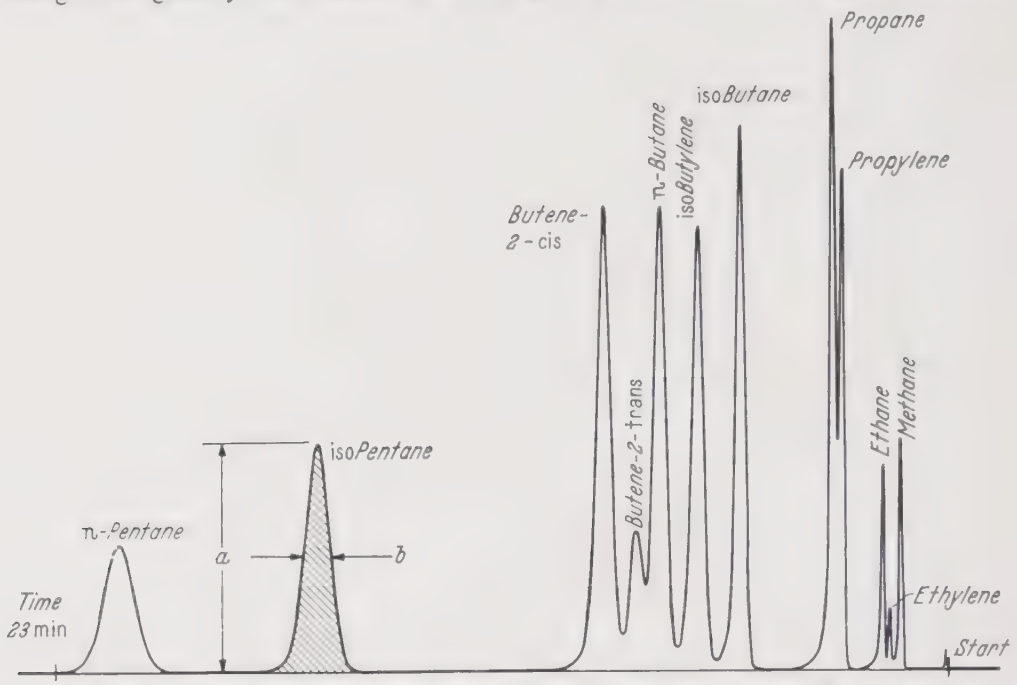

Figure 1. Trace from run on new Perkin–Elmer Vapor Fractometer. To find mole per cent *concentration of a component, area under peak is integrated by multiplying peak height* (*a*) *by half band width* (*b*)

Low boiling hydrocarbon mix having twelve components, 23 min *run at room temperature. Sample volume:* 1·5 c.c. (1 atm.). *Output:* $\frac{1}{4}$ *of available sensitivity. Carrier gas: helium. Flow rate:* 150 ml/min

conductivities 7 and 6, respectively), then the difference in thermal conductivity of various components would provide a maximum of 1–2 per cent difference in signal. This can generally be neglected where materials in a given chemical category will not exhibit differences in thermal conductivity of such magnitude.

Since the area under each peak is then directly proportional to concentration of each component (assuming an identical signal or response of each one of these components for the detector), the area relationship can be used for calculating relative concentrations of components present. Each peak area should therefore be determined on the run by integration or by multiplying peak heights by half band widths, *Figure 1.*

This procedure is somewhat inaccurate on sharp and narrow bands where band widths are small. In such cases, it might be preferable to multiply peak heights by retention times of the corresponding peaks since, to a first approximation, band widths are proportional to component speed and therefore to retention time. Errors may occur in this method of area calculation if viscosities in the gas phase of components differ largely, since band widths which are linked to speeds of diffusion will also be quite different.

The areas for all the peaks present are then added to give a total area which is normalized to 100 per cent. Therefore, the ratios of individual areas to this total give mole percentage concentration directly. Areas are not specifically more accurate than peak heights, but offer the advantage of providing results which are independent of instrument parameters. This is of considerable value, especially in quantitative data transfer from one instrument to another. Such a method also has the advantage of not requiring identification of all peaks in a given trace or any time-consuming calibration data. In other words, in this manner quantitative analysis can be made directly on each recording, without knowing instrument settings, identity of components present or components individual calibrating constants or plots. So far, this has never been achieved with other principles of analytical instrumentation.

(c) *Constant volume sampling*

At first sight, it would seem essential to control accurately the sample volumes introduced. In VPC the volumes required are very small (10–50 microlitres for liquids, 1–5 c.c. for gases) if recording time and column size are to be maintained at a minimum. However, for liquid samples the preceding two techniques do not require absolute volume control as long as mixtures can be injected into the system without change in composition. For gases, however, there always exists the danger that higher boiling fractions might condense in the syringe during the sample injection. This would ultimately result in a change of composition of the mixture to be analysed. In order to eliminate this difficulty it became necessary to design a by-pass system, which makes it possible to fill a chamber of known or calibrated volume with a sample without interference of the continuously flowing carrier gas stream. A 4-way valve is then thrown which directs the carrier gas through the sample volume chamber, thus carrying the entire sample on to the column without loss or change in composition. Such a valve and system is shown in *Figure 2* mounted on the side of the instrument (*Figure 3*).

The recording shown on *Figure 4* and the quantitative results obtained (*Table I*) on a standard Phillips sample illustrate the reproducibility and accuracy which can be obtained in this manner.

Table I. Analysis of Phillips Hydrocarbon Mixture No. 32
Model 154 Vapor Fractometer

Substance	*Run A*		*Run B*		*Phillips*
	Area	mole per cent	*Area*	mole per cent	mole per cent
Propane	26·4	2·56	26·4	2·56	2·55
iso*Butane*	247·1	24·00	247·5	24·05	23·98
n-*Butane*	756·0	73·44	755·4	73·39	73·47
	1029·5	100·00	1029·3	100·00	100·00

Figure 2. Constant volume sample valve

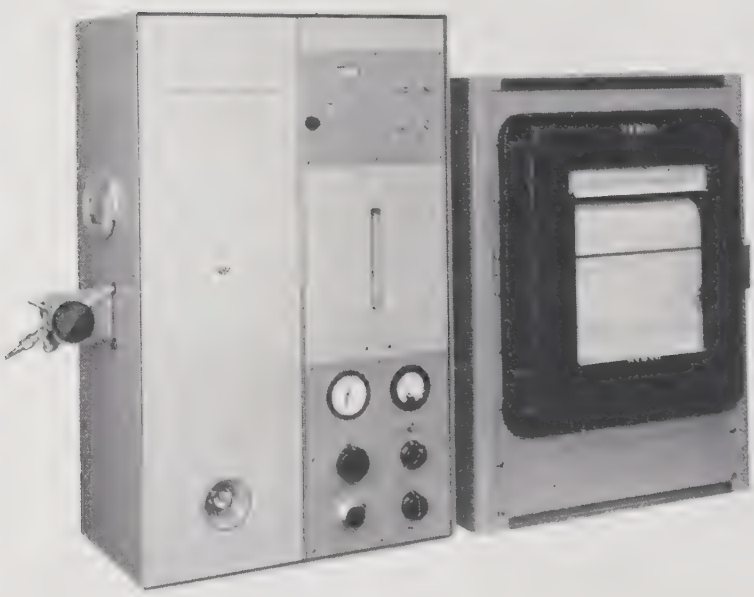

Figure 3. Instrument and mounted gas sampling system

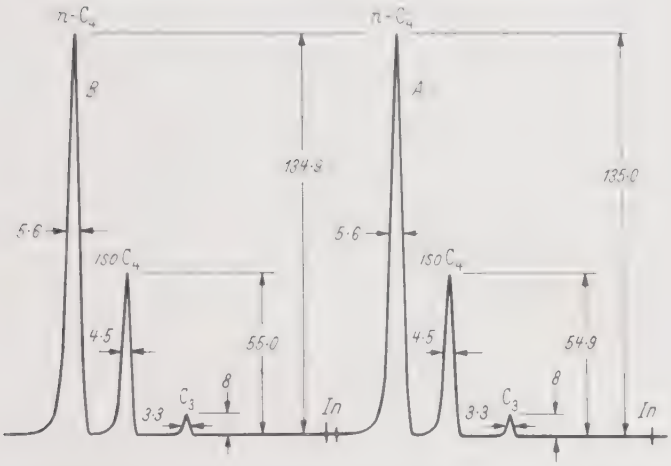

Figure 4. Recordings of Phillips hydrocarbon mixture No. 32, showing reproducibility obtained with Model 154 Vapor Fractometer

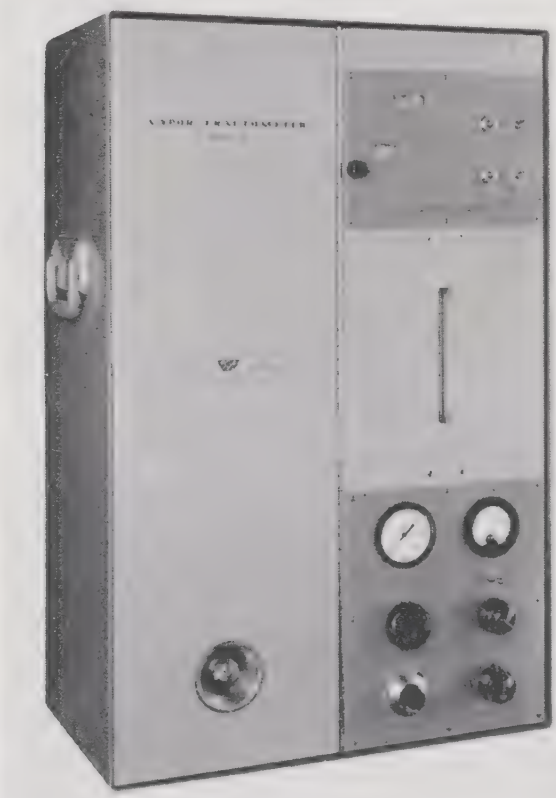

Figure 5. Perkin–Elmer Vapor Fractometer Model 154

It should be noted that the quantitative values of runs A, B and the Phillips analysis agree to a small fraction of one per cent.

These data were obtained on a commercial instrument (*Figure 5*) which differs from conventional designs by the use of a special thermistor-type thermal conductivity detector. The sensitive elements consist of microscopic glass-coated beads which are operated at a temperature considerably lower than conventional hot wire katharometers. This minimizes catalytic and thermal effects in the detector. The small size of the sensitive elements also permits reduction of the detector volume to a minimum thus increasing recording resolution and speed of response. Matching of the thermistor beads and design of a special bridge circuit also provided zero stability equal to or better than that of hot wire katharometers. Finally, increased sensitivity is obtainable since thermistors have considerably higher temperature coefficients of resistivity. The instrument is compactly housed in a small portable unit, which can be connected to any standard recorder.

Additional design features and applications have been discussed in an earlier paper: 'Vapor fractometry (gas chromatography), Part I', submitted to *Analytical Chemistry*.

DISCUSSION

See also page 432.

D. Ambrose: The effect of detector volume on the resolution of closely emerging peaks has been mentioned. In this respect the small volume of a thermal conductivity gauge made with thermistors is an advantage and resolution of peaks may sometimes be obtained when one only appears as a shoulder on the other with a wire gauge of larger volume.

C. M. Drew: I would like to make a few additional comments on the temperature programming. First of all I agree essentially with what Mr Hausdorff has said concerning the limitations of gas–liquid chromatography at both high and low temperatures. I should like, however, to make more clear the unusual features of this modified liquid–solid adsorbent, charcoal with suppressor on it, mentioned in my paper. The Shell people, in describing this packing, point out that they have occupied the non-linear portion of the absorption isotherm and have a homogeneous field of adsorption sites left over. The skew peaks characteristic of solid adsorbents such as untreated charcoal, then become almost symmetrical. There is also a very much more pronounced effect, which is quite useful, in that the temperature at which a peak appears is lowered by as much as 40–60 C. This means the packing may be used for the separation of high boiling materials. With a more stable tail suppressor on the activated charcoal I am reasonably certain that we could carry this right on up to the high temperature range much as has been described with the Apiezon L gas–liquid columns. Probably the most serious limitation to the programmed temperature scheme is the fact that you have to cool the column and then warm it through a temperature range. If you are interested in quick analyses, as in most control laboratories, this is very cumbersome. For that reason as I pointed out earlier we are using this method only for non-routine work.

J. A. Coles: I would like to draw your attention to *Figure 1* (page 380) which gives a trace of approximately a dozen components. I would like to ask Mr Hausdorff how he measures the half band width of the *trans*butene-2 peak. A possible alternative to the internal standardization method exists in the use of the product of retention time and peak height as a measure of concentration. What is the packing used on the column? Finally, I would like to compliment him, if I may have the honour, though I do not necessarily approve, on choosing Vapour Fractometry as a title.

If Dr Klinkenberg were to carry his argument a little further I think he would have to question chromatography as a term for the whole process. Maybe in Mr Hausdorff's column there is no darkening so it is undoubtedly not chromatography. I would like to ask if possible that at the end of the session a standard term be used rather than gas–liquid partition chromatography or vapour phase chromatography. Perhaps differential absorption is a possible one that may be called to mind. I offer that as a contribution.

G. R. PRIMAVESI: I should just like to protest strongly on Mr Hausdorff's remarks that we only use VPC as a research tool here. I have done about 99 per cent routine analysis and 1 per cent research and it seems as though he rather thinks we are in the back woods here and have only just heard of the thing. Believe me, I think most people have used it more for analysis than research. Also I think anybody could sample gases and get reproducible results, but when it comes to sampling liquid and putting on the same amounts it is a very different matter. I should like to know if anyone has yet thought of a satisfactory way of getting liquids on the column.

H. H. HAUSDORFF: First I would like to say that maybe I did not express myself well. I did not mean no quantitative analysis was being done in Europe, I meant the emphasis on quantitative analysis may be, to a certain extent, much stronger in the U.S.A. than it is here. As a matter of fact, in the beginning people looked at this method solely as a quantitative tool from a general point of view.

The second point in the order of questions is the problem about overlapping. You raise the question whether the *trans*butene-2 which was shown in the diagram could also be determined quantitatively. Of course it is quite difficult to measure the area when you have overlapping unless you extrapolate, but the method of using retention times instead of half band width can be applied to a certain extent. We have found in practice that when there is overlapping the accuracy is not too good.

G. J. MINKOFF: I would like to make two or three comments. The first one in a purely friendly spirit with regard to Mr Hausdorff's remarks as to what people in the U.S.A. were first interested in. If I may go back a couple of years, I lectured in a number of places on this subject, and the first comment was rather that they had never heard of it and were astonished at its power.

The second point deals with the use of thermistors. Now I am quite sure what I will say will be known to a good many people who have gone into this themselves, but perhaps a number of people like myself have at some time thought that it looked a very promising technique. I consulted somebody in a rather different field who had had a lot of experience of them and I got the impression that there were a number of points which were not commonly realized. The first thing is the question of sensitivity. One's immediate reaction is that the thing has a logarithmic response whereas the katharometer has only a linear response, so obviously one expects a lot more sensitivity. The first test is, those people who have used wire katharometers with proper amplification get the same sort of sensitivity as with the thermistor type within a matter of two or three, or perhaps ten. But we are really expecting a difference of the order of hundreds, perhaps thousands. One of the reasons apparently, according to this particular informant, is that when you are using a thermistor and want to get stable results you can only use a temperature difference perhaps of the order of 1°C, whereas of course with a wire you can go much higher, so that immediately you are throwing away a lot of the thermistor's advantage.

The third point is with regard to high temperature working. This is not so important at room temperature or perhaps up to 150°C as Mr Hausdorff's instrument operates, but if people are going up to, say, 300°C then the response drops, the sensitivity drops, in other words the slope of the resistance/temperature plot drops quite sharply with increasing temperature. Also it is very difficult here, at

least, to get thermistors which match not only in response but in temperature coefficient of response. The two properties are interrelated, but it is very difficult without doing a lot of tests to sort them out.

A further consequence of the very rapid change of resistance with temperature is that if you go up to a high temperature with the same detector the resistances in your bridge will be heavily overloaded in one direction and you will have to have quite an elaborate set of compensating devices to ensure that it is working at its optimum sensitivity when the resistances are all equal on the four sides.

One final point in connection with measuring areas. Someone has mentioned to me, and it seems rather a snag, that with the first few peaks that come out it is quite easy to measure the height, but what is the precision in measuring a half width of perhaps 1 mm? Should there not be some system whereby the recorder is run more quickly over the first part of the chromatogram?

N. G. ADAMS: This is in answer to Dr Primavesi's question about introducing small quantities of liquids. I have a special syringe for doing that which is very simple and is shown in *Figure 6*.

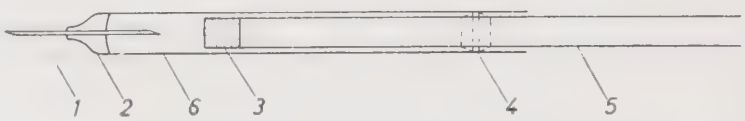

Figure 6. Liquid sampler for gas chromatography
(4/10 full size)

1, Double pointed hypodermic needle; 2, No. 29 Sauereisen cement; 3, Neoprene rubber plug cut with No. 4 cork borer; 4, Three bands cut from $\frac{1}{8}$ inch *surgical rubber tubing; 5, Glass tubing* 8·0 mm *outside diameter; 6, Glass tubing* 11·6 mm *outside diameter*

The hypodermic needle (*1*), sharpened at each end, is sealed through the end of glass tube (*6*) with No. 29 Sauereisen cement (*2*). A Neoprene plug (*3*) is cut from a new laboratory stopper and inserted into the end of glass tube (*5*). An airtight seal (*4*) is formed from three short lengths of $\frac{1}{8}$ inch surgical rubber tubing stretched around tube (*5*) and lubricated with silicone stopcock grease. One piece $\frac{1}{16}$ inch wide is placed on tube (*5*) and two pieces $\frac{3}{8}$ inch wide are placed over it, preventing the smaller one from rolling as tube (*5*) is moved inside tube (*6*). A small rubber suction bulb (not shown) is placed over the end of tube (*5*) to provide a partial vacuum for filling the needle.

Operation of the syringe is as follows:

(*A*) Slide tube (*5*) to the right (looking at the drawing) until (*4*) is at end of tube (*6*).
(*B*) Seal the left end of needle (*1*) by inserting it into a rubber stopper.
(*C*) Slide tube (*5*) to the left until needle pierces completely through plug (*3*). This step compresses air in the chamber between tubes (*5*) and (*6*).
(*D*) Remove stopper from left end of needle and dip needle in liquid sample.
(*E*) With suction bulb (not shown) draw sample through the needle into tube (*5*).
(*F*) With needle still immersed in the liquid, slide tube (*5*) to the right until the inner tip of needle is completely enclosed in plug (*3*). This seals one end and holds the sample in the needle.
(*G*) Remove needle from sample bottle and thrust it through the rubber disc in the sample introduction port on the instrument, after venting the carrier gas pressure.
(*H*) Slide tube (*5*) to the right slowly until tip of needle barely emerges from the plug (*3*). At this point the air compressed in chamber (*6*) is released through the needle, blowing the liquid sample out of the needle into the inlet port. In the original design, the airtight seal (*4*) was omitted, along with operation steps (*B*) and (*H*). The sample merely flashed into the evacuated chamber during step (*G*).

(*1*) Tube (*5*) is rinsed with solvent, removed from tube (*6*), turned end-for-end, re-inserted into tube (*6*), and the needle is inserted through a rubber cap into an auxiliary vacuum system. This constitutes the cleaning procedure to prevent possible contamination of subsequent samples. When the plunger is inverted it should be pushed all the way into tube (*6*) to prevent breakage when evacuated.

This syringe was a modification of a device which was used to introduce small samples into a mass spectrometer. The original design was to introduce a sample into a vacuum and our modifications have been merely to introduce a sample to atmospheric pressure. The original sampler was described at the mass spectrometer meeting in San Francisco last year. As to reproducibility, which I am sure you are interested in, I ran five successive runs of acetone with this device and calculated the standard deviation on both the areas and the peak heights, and the standard deviation for the peak heights was 0·79 per cent, and for the areas, 0·85 per cent. This represents the reproducibility of the sampler and the chromatographic instrument together, which we feel is quite adequate for quantitative analyses.

32

THE QUANTITATIVE ANALYSIS OF MIXTURES OF CHLOROFLUOROMETHANES

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Research Laboratory, Imperial Smelting Corporation Limited

Gas–liquid partition chromatography has been applied to the analysis of mixtures of the chlorofluoromethanes and carbon tetrachloride. The mixture was eluted by nitrogen from a column packed with kieselguhr impregnated with dibutyl phthalate. Samples were measured in the vapour state, and calibration was carried out using pure components. A linear relationship between peak height and sample volume at s.t.p. was obtained. The accuracy and reproducibility were found to be better than 1·5 per cent absolute.

Gas-liquid partition chromatography has been applied to the separation and quantitative estimation of mixtures of the monochlorotrifluoro-, dichlorodifluoro- and trichloromonofluoro-methanes and carbon tetrachloride. The boiling points of these compounds are −81, −30, +24 and +76°C, respectively, and the initial problem was to find a partition column capable of separating the two lower boiling components and from which carbon tetrachloride could be eluted in a reasonable time. This was solved by using a column fitted with an additional take-off half-way along its length. It was packed with kieselguhr impregnated with dibutyl phthalate, and the components leaving the column were detected by means of a thermal conductivity cell.

The composition of a mixture was determined by measuring the heights of peaks recorded by a potentiometer, and calculating the quantity of each component present from calibration curves which were obtained by putting known volumes of the pure components through the column. Reproducibility tests have been carried out and individual results found to agree within 1·5 per cent absolute.

Experimental

Apparatus

The apparatus consisted of three main parts:

(*a*) the column
(*b*) the thermal conductivity cells
(*c*) the sample measuring pipette.

(a) *The column*—A diagram of the column is shown in *Figure 1*. It was U-shaped and constructed from two 45 cm lengths of 4 mm bore tubing, joined with capillary tubing. An additional capillary take-off was connected as shown and both column exits were fitted with taps (T_4, T_5) so that nitrogen could be passed through either the whole or half the column.

The packing used was kieselguhr (Celite 545) prepared as described by James and Martin[1] and impregnated with dibutyl phthalate. (Ratio of liquid phase to Celite 1 : 2·2 by weight.)

A jacket heated by trichloromonofluoromethane vapour (24 C) surrounded the column, and a water condenser was used to condense the vapour.

(b) *The thermal conductivity cells*—Glass thermal conductivity cells (*Figure 2*) were kept at a constant temperature of 25 C in a thermostat. These cells were constructed from 8 mm bore Pyrex tubing as follows. A 5½ in. length of platinum wire, of 0·002 in. diameter, was joined to 20 s.w.g.

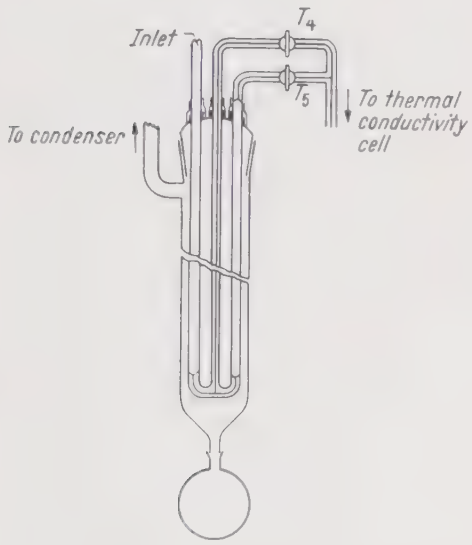

Figure 1. The column

Figure 2. Glass thermal conductivity cell

platinum wire by drilling a short hole along the length of the thicker wire at one end. The 0·002 in. wire was inserted and fixed by squeezing the end of the thicker wire. This method was found to give a stronger join than either spot welding or silver soldering. The thicker platinum wire was sealed into the glass tubing, the capillary inlet and outlet attached and the platinum wire pulled taut by softening the glass tubing. The lower platinum wire was welded to a length of copper wire which was enclosed in a glass tube bent so that the electrical connections could be made at a convenient position above the thermostat bath.

The two cells each had a resistance of about 8 ohms and were connected in a Wheatstone bridge circuit. The other two fixed resistances were 10 ohms each and made from 'Minalpha' wire. A 0–5 mV recording potentiometer was used to measure the out-of-balance potential of the bridge.

(c) *The sample measuring system*—The gas pipette (*P*) used for measuring sample volumes is shown diagrammatically in *Figure 3*. A single-way (T_2) and two-way (T_1) solid plug 2 mm tap were connected by a 12 cm length of approximately 5-mm bore tubing, which formed the calibrated volume (2·6 ml) for the measurement of sample volumes. The two-way tap was connected to a manometer and vacuum line and also to the nitrogen supply.

General

A schematic diagram of the apparatus is shown in *Figure 3*. A nitrogen cylinder (*N*) fitted with a standard reducing valve was connected to an on–off valve (V_1) and a phosphoric acid bubbler (*B*), to maintain a constant inlet pressure to the column of about 10 cm of mercury. The nitrogen leaving the valve V_1 was passed through an orifice flowmeter (*F*), thermal conductivity cell (D_1) and two-way tap (T_3). This tap was connected to the column and to tap T_1 as shown. Thus the nitrogen could be passed either directly through the column or through the column via the sampling pipette. Samples were

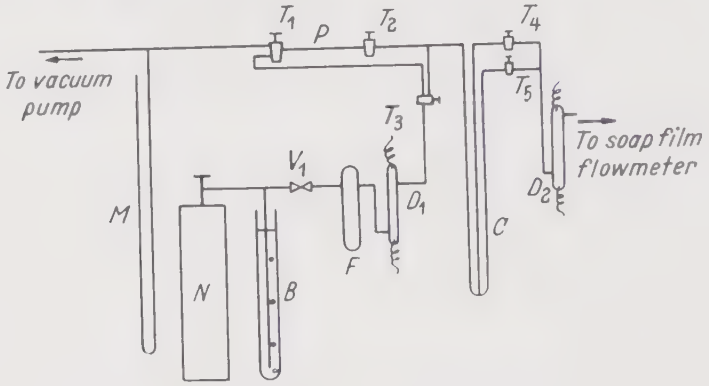

Figure 3. Schematic diagram of apparatus

measured under reduced pressure in the tube of known volume connecting the two-way and single-way taps T_1 and T_2 respectively. Tap T_1 was also connected to a mercury manometer (*M*) and vacuum line through which the samples were introduced. The column (*C*) was connected to a second thermal conductivity cell (D_2), and a soap film flowmeter was attached to this cell to measure the nitrogen flow rate.

The solubility of the chlorofluoromethanes in 'Apiezon' and 'Silicone' high vacuum greases made these unsuitable for lubrication of the taps. A grease which has previously been described[2] for use with tetrachlorethylene was employed. This grease is a mixture of mannitol, dextrin and glucose in the proportions 3·5 : 7 : 18 respectively.

Operating procedure

The following procedure was adopted for the analysis of a mixture of the three chlorofluoromethanes and carbon tetrachloride, the sample being contained in a 1 litre flask at a pressure of approximately half an atmosphere.

The flask was connected to the vacuum manifold and all connecting lines, including the gas pipette, were evacuated, using a rotary oil pump. The flask was then opened until the required pressure (usually about 20 cm of mercury) was shown by the manometer *M*. (It was not necessary to read this pressure accurately since the total volume of sample was determined from the recorder trace.) During this operation taps T_3, T_4 and T_5 were in such positions that the nitrogen passed through the whole column. Tap T_1 was now closed, tap T_3 then T_1 opened so that nitrogen passed into the gas pipette. When the pressure had risen to the column operating inlet pressure, shown by a zero

flowmeter reading, tap T_2 was opened and the sample carried on to the column in the nitrogen stream at a flow rate of about 20 ml/min.

Under these conditions after three minutes the monochlorotrifluoromethane and the dichlorodifluoromethane had been eluted from the column.

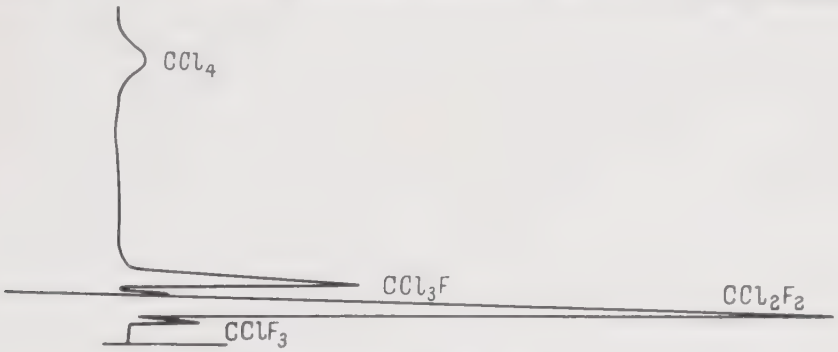

Figure 4. Chromatogram of four-component mixture

The positions of taps T_4 and T_5 were then reversed so that nitrogen flowed through half the column. This produced a 'kick' in the recorder trace (see *Figure 4*) but did not affect the base line position, although because of the reduced pressure drop in the system the flow rate had increased to 42 ml/min.

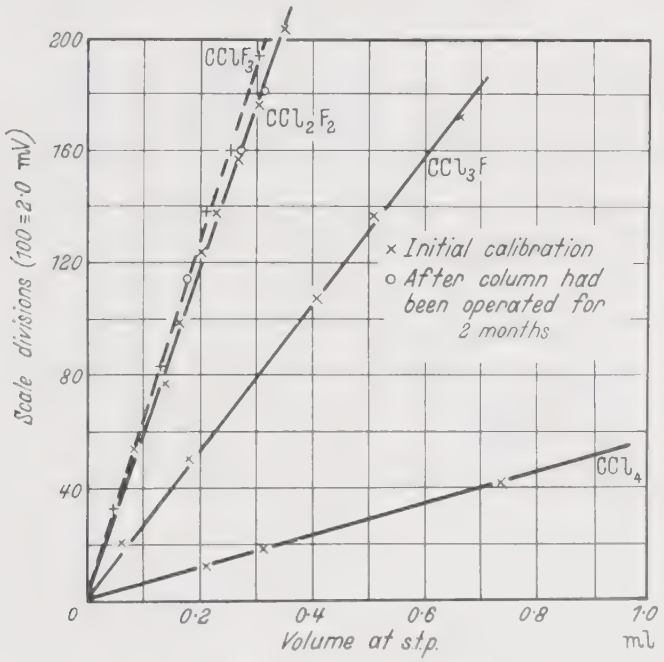

Figure 5. Calibration curves

The trichloromonofluoromethane started to leave the column after a total time of three and a half minutes and the analysis was complete in 25 minutes.

A typical trace is shown in *Figure 4*, from which the peak heights for each component were measured and the composition of the mixture calculated from calibration curves obtained by using the pure components of the mixture as described below.

Calibration

The column was calibrated by filling the gas pipette to a known pressure with a pure component, passing the latter on to and through the column as described above and measuring the peak height obtained. This was repeated, filling the pipette to different pressures, and the peak height obtained was plotted against volume at s.t.p. of component. A linear relationship was found for each of the components as shown in *Figure 5*, and checks of the calibration for dichlorodifluoromethane after the column had been in continuous daily use for two months showed very good agreement with the original line (see *Figure 5*).

Results

Experiments have been carried out to establish:

(*a*) the reproducibility of the method

(*b*) that the calibration of peak height against quantity of a component for pure components applies in the case of mixtures

(*c*) that the use of different amounts of a given mixture for analysis is without effect on the results.

(a) *Reproducibility*—The results obtained from duplicate determinations on four different samples of four-component mixtures are shown in *Table I*.

Table I

Sample No.	*Composition* vol. %			
	$CClF_3$	CCl_2F_2	CCl_3F	CCl_4
97	4·3	77·0	17·0	1·7
	4·0	77·0	17·5	1·5
259	0·3	69·5	22·3	7·9
	0·3	70·0	21·2	8·5
275	3·7	76·5	15·2	4·6
	3·7	77·5	13·7	5·1
303	4·5	81·2	9·1	5·1
	4·4	81·8	8·6	5·2

(b) *Calibration*—Mixtures of CCl_2F_2 and CCl_3F were made up from the pure components and then the composition determined. The comparison of observed and actual compositions is given in *Table II*.

(c) *Influence of quantities used*—The volume at s.t.p. of samples of a given mixture put through the column were varied by a factor of three; the results of the composition of the mixture in each case are compared in *Table III*.

Review

The gas pipette and the method of measuring samples described above have advantages, particularly for calibration purposes, over methods published by other workers[3–5]. These methods have included: the injection of approximately equal volumes of known mixtures of gases diluted with nitrogen from

a hypodermic syringe, and the use of a gas pipette similar to that described in this paper but which was filled by passing a sample through. For calibration it was necessary either to make up known mixtures or to use several

Table II

Composition vol. %			
Actual		*Observed*	
CCl_2F_2	CCl_3F	CCl_2F_2	CCl_3F
33·9	76·1	33·8	76·2
54·0	46·0	53·8	46·2
58·0	42·0	58·0	42·0
76·8	23·2	77·6	22·4
87·2	12·8	88·2	11·8

pipettes of different volumes and to apply corrections to the relation between peak height and amount of sample when analysing mixtures.

The advantages of the method described are:

(*i*) Pure components are used and since each sample is brought to the column inlet pressure by admitting nitrogen before being put on the column, the total volume of sample plus nitrogen is always constant, irrespective of

Table III

Volume of sample ml *at s.t.p.*	*Composition* vol. %	
	CCl_2F_2	CCl_3F
0·685	65·0	35·0
0·566	64·5	35·5
0·506	64·8	35·2
0·453	64·2	35·8
0·317	64·4	36.6
0·218	64·0	36·0

the volume at s.t.p. of the component measured. The peak height given by a certain amount of a component is therefore the same whether it is measured as a single component or in a mixture. The analysis of mixtures can be carried out using the relation between peak height and quantity of a component obtained by calibration without applying any corrections or measuring peak areas instead of peak height as described by other workers.

(*ii*) The size of a sample can be varied.

(*iii*) Substances boiling at about room temperature, which cannot be injected easily as liquids from a micrometer syringe, can be handled as vapours without difficulty. In addition, substances boiling above room temperature but having appreciable vapour pressures, e.g. carbon tetrachloride, can be treated in the same way.

(*iv*) Samples contained in vessels at pressures below atmospheric can be analysed without risk of dilution with air.

The results given in *Tables I*, *II* and *III* show that (*a*) the reproducibility of the method is better than 1·5 per cent absolute even for the least sensitive component, (*b*) the calibration using pure components is applicable to mixtures and (*c*) the results are independent of the amount of sample admitted to the column over the volume range 0·2–0·7 ml at s.t.p.

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33

APPLICATION OF GAS–LIQUID PARTITION CHROMATOGRAPHY TO SOLVENT ANALYSIS

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In the analysis of solvents the technique of gas–liquid partition chromatography has been found to be most useful. The procedures of identification and quantitative determination used in connection with solvent analysis when thermal conductivity is being used for detection are described. The importance of selective stationary phases is illustrated in the analysis of hydrocarbon solvents and mixtures of oxygenated compounds. Combination of the fluorescent indicator liquid phase adsorption chromatographic technique with gas–liquid partition chromatography has been used for certain complex solvents. A larger scale gas–liquid partition chromatographic unit has been used for separating constituents from complex solvent mixtures for identification.

SINCE the introduction of gas–liquid partition chromatography (GLPC) by James and Martin[1] in 1952 the technique has been found outstandingly useful in a large number of industrial laboratories in this country and in fact throughout the world. Several papers[2–8] have been published illustrating the versatility of the technique in the analysis of volatile liquids and gases. The GLPC apparatus described in this paper has been based on that of Ray[9]. The only limitation of this apparatus has been the need to calibrate for quantitative work. This is no great disadvantage in view of the rapidity with which separate runs and calibration can be carried out. Many varied analytical problems encountered in applicational research in the petroleum industry have been solved successfully, and sometimes surprisingly rapidly, with the aid of or entirely by GLPC. The field of solvent analysis has been selected as an illustration of how the technique has saved time and enabled accurate analysis to be obtained where this previously would have been impossible or far too laborious. The identification and determination of the main constituents of solvent mixtures could take anything up to four months by previously available techniques of distillation, organic group analysis and spectroscopy. Many of the minor constituents could not be determined and results were often far from reliable. GLPC has altered this picture enormously. It is now possible to separate the individual constituents of solvent mixtures completely in a matter of hours and often to identify and determine quantitatively these constituents. Even very complex mixtures can frequently be resolved provided initial separation into types has been carried out, for example, by the liquid phase fluorescent indicator adsorption technique of Ellis and Le Tourneau[10].

The selectivity of the GLPC technique is such that type separation can also be carried out with certain samples by suitable choice of stationary phases[11] and some examples are described later. With higher boiling samples the choice of stationary phases becomes limited owing to the difficulty, amongst others, of obtaining polar liquids which are of suitable stability and low volatility. However, it has been possible to carry out a limited separation of substances boiling at as high as 350° C using silicone fluids or high vacuum grease as stationary phase, although in the author's laboratory the highest boiling substance analysed so far has been C_{12} alcohol boiling at 260° C. Thus the only limitation to the type of solvent which can be analysed by GLPC is the final boiling point which at the present time cannot exceed about 300°C. This covers all the more common solvents and the solvent mixtures.

Techniques and Apparatus

Frequently when dealing with a solvent sample information is available concerning the possible constituents and boiling range. Generally as a preliminary the whole sample is run through a GLPC column containing a polyethylene glycol or dinonyl phthalate liquid stationary phase to obtain some idea as to the complexity. If the sample is reasonably simple and the class of compounds present is known it is possible to proceed directly to identification and quantitative determination by GLPC. This stage is considered in more detail later. For complex solvent mixtures the analysis can be considered in three stages:

Stage 1: Routine tests

Element analysis for carbon, hydrogen, oxygen, nitrogen, sulphur and halides.
Distillation range.
Organic functional groups.
Acid value, saponification value, carbonyl value, active hydrogen and any other determinations considered necessary in view of the elemental analysis.
Preliminary GLPC run.

Stage 2: Type separation and determination

The total oxygenated and other polar compounds are determined by means of the fluorescent indicator adsorption (FIA) technique developed by Ellis and Le Tourneau[10]. 0·75 ml of sample is used with activated Davison silica gel packed in a long narrow column. The sample is either pre-treated with the fluorescent indicators or a small plug of silica gel treated with the indicators is added to the column. The sample is displaced down the column with *n*-butylamine and separates into paraffins, olefins, aromatics and oxygenated compounds, plus compounds of similar adsorption affinity. On irradiating the column with u.v. light the separate zones of compounds are revealed by the various fluorescent indicators. By measuring the lengths of the zones the quantities of the various classes of compounds mentioned are obtained. The accuracy of the results is about $\pm 2{\cdot}0$ per cent based on the original sample.

It has been found, however, that the lower ketones and alcohols apparently tend to be partially by-passed by the butylamine. This, however, is not important for quantitative results since in these cases an assumed total length

for the whole sample can be used. It is advisable to carry out such determinations in duplicate to ensure that the correct amount of sample has been added to the column. A slight improvement in technique has been to have a layer of Celite at the top of the silica gel and to inject the sample into the Celite with a hypodermic syringe. The initial heat of adsorption on silica gel frequently causes loss of the more volatile constituents of the sample and this is avoided by using the above technique. It has been noted on occasions that the oxygenated compounds are split into two zones which are made visible by a brown ring at the interphase. Analysis of these zones by GLPC has revealed esters in the lower zone (least adsorbed) and alcohols and ketones in the upper zone.

Figure 1. Sample collecting system for analytical fluorescent indicator adsorption columns

The FIA technique has been used successfully to prepare samples of the different compound types for GLPC analysis. This separation into compound types is essential for the more complex hydrocarbon solvents and oxygenated solvents. When the amounts of sample available were limited, the small analytical FIA columns were adapted to enable the various fractions to be collected from 0·75 ml of sample. The end of the column was ground to take a hypodermic needle and the fractions collected in a small cooled tube sealed with a serum cap, as shown in *Figure 1*. However, when larger samples were available the column size was increased as shown in *Figure 2*. 15 ml of sample can be successfully fractionated in this column.

Between the various zones there is always a small interphase of mixing. This interphase must be rejected and is generally so small that it can be neglected. If, however, it is essential to collect an absolutely representative sample of any particular group, this can be done by diluting the sample with

single pure substances which are located in the zones of the chromatographic separation before and after the particular group required. It must be established that these substances do not interfere in the GLPC analysis of the particular group of compounds being considered. Thus if the dilution has been sufficient the interphase zones can be collected and the substances which have previously interfered in the GLPC analysis will be undetectable.

Figure 2. Comparison between an analytical fluorescent indicator adsorption column and a larger column of this type

The absolute limit of boiling point for wide range hydrocarbon mixtures which can be successfully separated by the FIA technique is 315°C. When oxygenated compounds and other substances of similar adsorption characteristics have to be separated the limit of boiling point has not been established but is probably lower than 315°C.

Stage 3: Identification and determination of the solvent constituents by GLPC

The GLPC equipment was basically similar to that used by Ray[9]. The layout is shown diagrammatically in *Figure 3* and a photograph of the smaller unit used is shown in *Figure 4*. It will be seen that the arrangement of the thermal conductivity cells or katharometer is different from that of Ray.

Both the cells are situated on the outlet side of the column with a cold trap between them. It was found with this arrangement that better stability was obtained and the apparatus was practically insensitive to pressure changes on the inlet side of the column.

The katharometer was a copper cylinder $5\frac{1}{4}$ inches long and $2\frac{1}{2}$ inches in diameter. Two chambers of $\frac{1}{8}$-inch bore, containing the sensitive platinum elements, were drilled parallel to the longitudinal axis of the block. The platinum elements were 50 s.w.g. (0·001 inch) wires, tensioned at one end by springs made from platinum–rhodium wire.

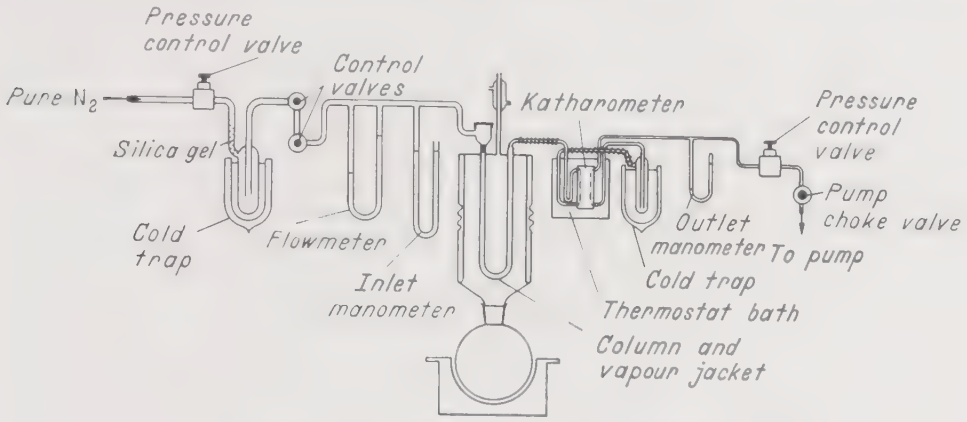

Figure 3. Flow diagram of GLPC apparatus

Two GLPC units have been used for solvent analysis. One unit was the normal analytical scale taking sample sizes between 0·01 and 0·04 ml with glass columns of 6 mm internal diameter and 184 cm length enclosed in a vapour jacket for temperature control. Samples were introduced into the column through a serum cap by means of a hypodermic syringe. The katharometer of this unit was immersed in an oil thermostat bath and maintained at such a temperature that high sensitivity was attained, but no condensation of the constituents being analysed took place. An important point to note is that with increasing katharometer temperatures there is a fall in sensitivity due to the thermal conductivity of most substances approaching that of nitrogen, and indeed becoming higher than that of nitrogen if the temperature is taken high enough. There is consequently an optimum katharometer temperature for the greatest sensitivity for each type of sample analysed when nitrogen is used as the mobile phase. It is also possible to make the katharometer insensitive to certain compounds by choice of temperature.

The other GLPC unit was considerably larger and was fitted with a glass column of 12·7 mm internal diameter and 830 cm length enclosed in an electrically heated air furnace with forced air circulation. The katharometer was heated by an electric heating tape. A manifold trap system was located between the two katharometer cells so that constituents in the gas stream leaving the column could be isolated for further identification. With small samples sizes this larger unit is capable of a high degree of resolution but so far it has mainly been used for isolating hydrocarbon constituents of solvents for the purposes of identification. A sample size of 0·5–3 ml was used in these circumstances.

The recorder used with both units gave a full scale deflection for 2·5 mV with a 12-inch chart.

Carrier for stationary phase—Diatomaceous earth, Celite 545, with the fines removed was used in the smaller columns. Sterchamol furnace brick, ground and sieved to suitable mesh sizes (44–52), was used for the larger column.

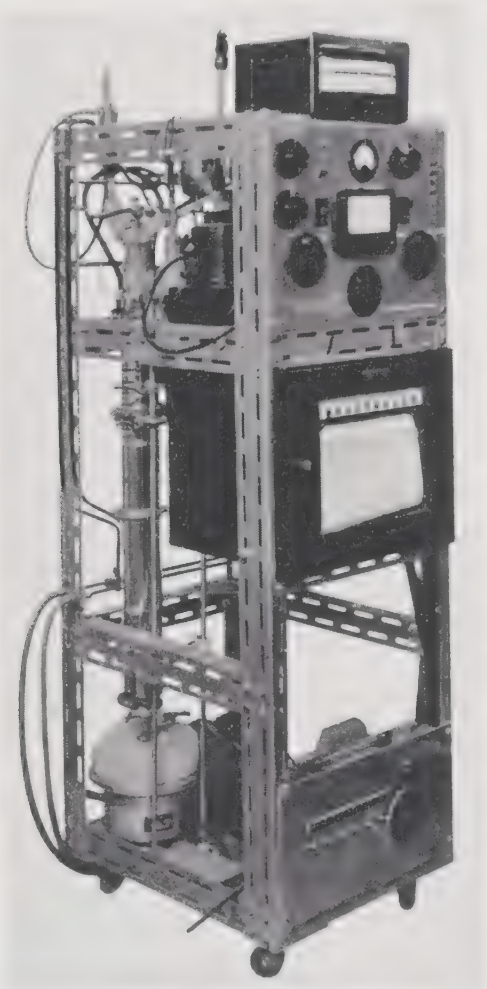

Figure 4. GLPC unit used for solvent analysis

Stationary phases—Mainly the following stationary phases have been used for solvent analysis:

Paraffin hydrocarbon (medicinal oil of average C_{29} carbon number) Maximum column temperature 120 C at 35 mm of mercury outlet pressure. Used mainly for the separation of oxygenated compounds.

Dinonyl phthalate (DNP). Maximum column temperature 140 C but 35 mm of mercury outlet pressure. Good general purpose stationary phase but not suitable for aqueous solvents.

Fluorene picrate. Maximum column temperature 110 C at 70 mm of mercury outlet pressure. Especially useful for the separation of aromatics.

Polyethylene glycols. 400 and *600**. Useful for the separation of oxygenated compounds and water (maximum temperature of operation not determined).

Silicone Fluid MS. 550. Useful for the separation of higher boiling substances (maximum temperature of operation not determined, but has been used at 220°C with 100 mm of mercury outlet pressure).

None of the above stationary phases has been found to be ideal and columns have been found to change gradually in constant use under the conditions of operation described, i.e. gas drawn through the columns by a vacuum pump with outlet pressures varying between 35 mm and 200 mm of mercury.

Mobile phase—Pure nitrogen gas (oxygen free) has been used invariably as the mobile phase. This was dried by passage through activated silica gel and a liquid air trap.

Identification—With simple solvents a knowledge of the likely impurities is sometimes available and the retention volumes of the various peaks can be checked against those of the particular suspected compounds. Final identification is always carried out by adding the suspected substance to the solvent and re-running the sample to see if the peak height has increased.

With more complex mixtures, or even simple solvents about which little is known, the initial identification is carried out by running the sample on two or three stationary phases with different solubility characteristics, e.g. paraffin phase, DNP phase and polyethylene glycol phase for oxygenated compounds. The relative changes in the retention volumes on the different stationary phases will give many indications as to identity, especially when used in conjunction with the organic group analysis of the original sample.

If identification is still not possible, the particular constituents are condensed from the gas stream on the small or large GLPC units and examined by spectroscopic techniques or other procedures. This latter method is also used if no reference compound is available for re-running with the original sample. Retention volumes or times are obtained by measuring from the injection point (corrected for column dead-space) to where the tangent to the slope of the rear of a peak intersects the base line. This has been found to be more independent of concentration of the constituent than some other methods.

It is difficult to lay down any definite method for choice of column temperature for an analysis, but if the boiling range of the sample is known, the initial run is best carried out at 20–30C° below the temperature at which 95 per cent of the sample distils. The complexity of the sample and the degree of separation revealed in this run can then be utilized to decide what column temperature to use for identification and quantitative determination of the constituents. When initially separating unknown samples on selective stationary phases like polyethylene glycol, it is advisable to allow the column to run for at least two hours to ensure that all the substances have been eluted. It is sometimes necessary to carry out analyses at two column temperatures if the sample is particularly complex and of wide boiling range.

Quantitative estimation—The following techniques have been used:

(*1*) *Addition to sample.* A known amount of each constituent is added in

* Polyethylene glycol 400 is a polymer containing approximately nine units of glycol ($CH_2 \cdot CH_2 \cdot O$) and polyethylene glycol 600 contains approximately fourteen units.

urn to the original sample and run through the apparatus. From the increase in peak height the concentration in the original sample is estimated. A correction for any difference in sample size is applied from the relative peak height of one of the other constituents. This procedure can conveniently be carried out in conjunction with the identification. The accuracy of the analyses is about ± 5 per cent when this method is used.

(*2*) *Internal standard* (*or marker*). For the accurate determination of substances in quantities up to 10 weight per cent the use of an internal standard is preferred. Blends of known composition, each of which contains the same proportion of the standard, are prepared and run through the GLPC apparatus. The calibrations are then made relative to this standard and the sample is also run with the standard to obtain the quantitative values. This procedure is unsuitable for complex mixtures because of the difficulties of finding a standard. This is the most accurate of all the methods, ± 1 per cent being easily achieved.

(*3*) *Areas*. The area of each peak on the chromatogram relative to the total area of all the peaks has been used quantitatively. It is necessary to multiply each area by a factor which is determined from blends of known composition run under the same conditions. When using area approximations such as (height × width at half height) the accuracy that can be achieved is about ± 2 per cent.

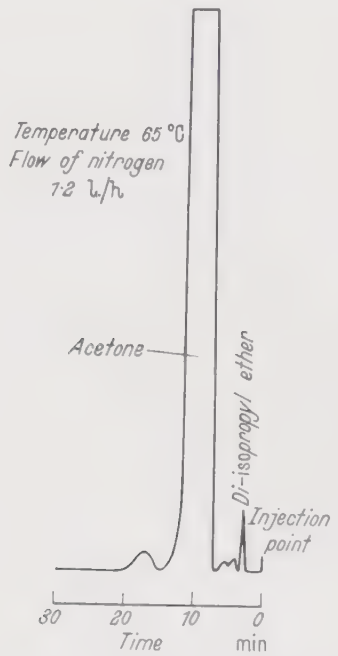

Figure 5. Industrial acetone trace using polyethylene glycol 400 column

Some Typical Examples of Solvent Analysis

Simple solvents

Industrial acetone—The determination of impurities in industrial acetone illustrates the sensitivity of the GLPC technique. Using a polyethylene glycol 400 column at 65 °C four minor impurities were detected. The trace is shown in *Figure 5*. Only the first of these impurities was identified and this was

*iso*propyl ether. The amount determined was 0·08 volume per cent and it would be possible to detect 0·01 per cent under the same conditions. A wire current of 120 mA was used in the katharometer and a somewhat larger sample size (0·04 ml) than used for the normal analytical scale apparatus (cf. 75 mA and 0·025 ml). This by no means represents the limit of sensitivity since it has been shown to be possible to increase this by a factor of about 60, with hydrogen as the mobile gas.

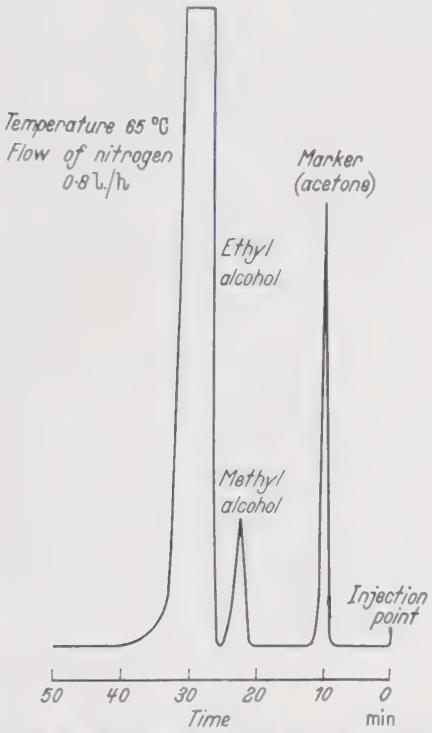

Figure 6. Determination of methyl alcohol in methylated spirit using a polyethylene glycol 400 column

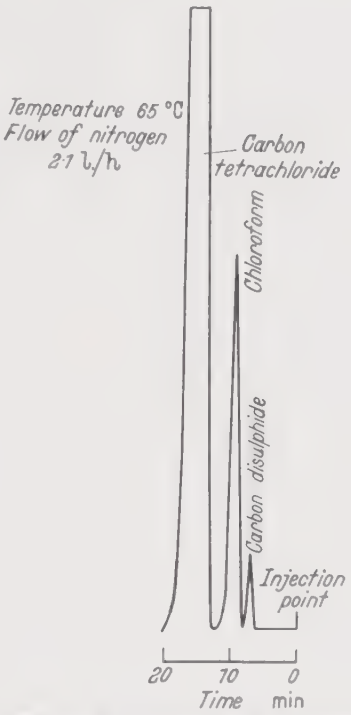

Figure 7. Impurities in industrial carbon tetrachloride determined on a paraffin column

Industrial methylated spirit—The determination of methyl alcohol in IMS can be carried out on a polyethylene glycol 400 column. Acetone is used as marker. A typical trace is shown in *Figure 6*. The sample contained 4·6 volume per cent of methyl alcohol.

Industrial carbon tetrachloride—Impurities in industrial carbon tetrachloride were identified and determined on a paraffin column. These were estimated approximately by the addition technique as 1·2 volume per cent carbon disulphide and 10 volume per cent of chloroform. The trace is shown in *Figure 7*.

Hydrocarbon solvents

Petroleum spirit—The determination of small amounts of aromatics in petroleum spirit was carried out, using a stationary phase of fluorene picrate. The paraffins passed rapidly through and were bunched together at the beginning of the chromatogram (see *Figures 8* and *9*) whereas the aromatics were well resolved. The internal standard technique was used to

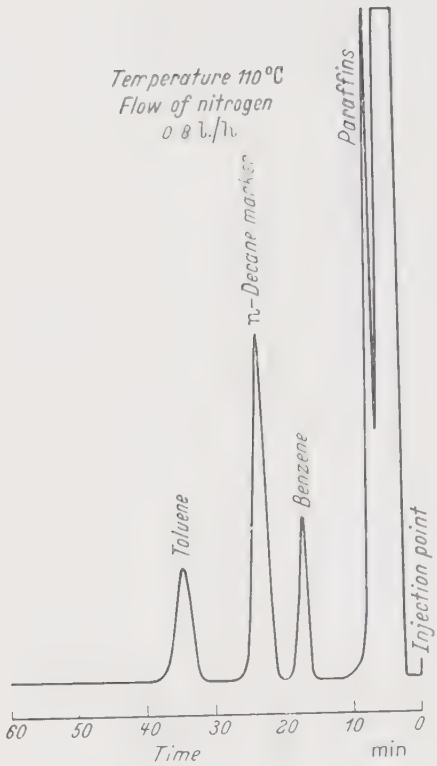

Figure 8. Resolution of aromatics in petroleum spirit. Boiling range 80–110°C

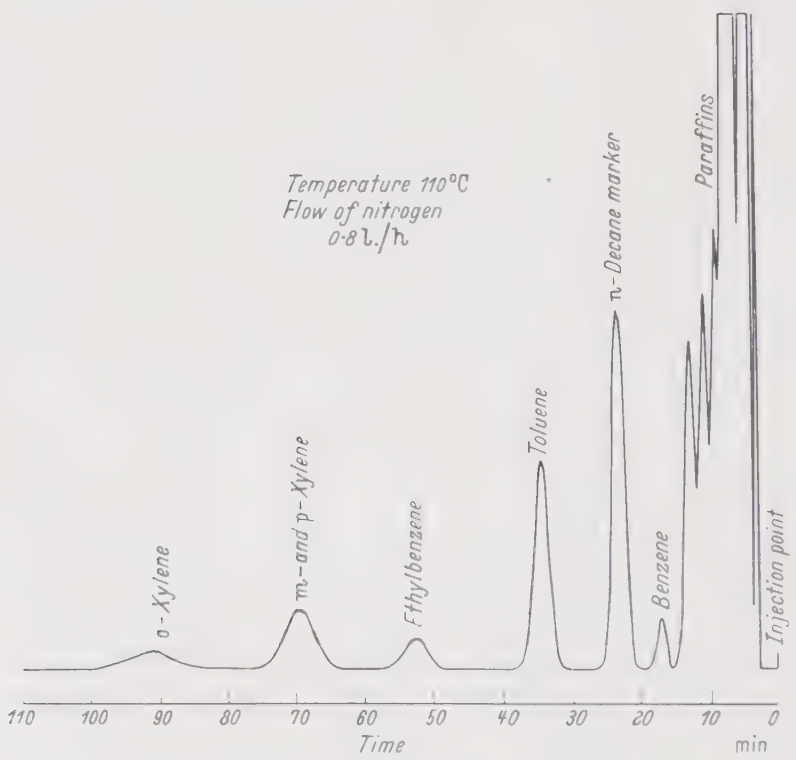

Figure 9. As Figure 8 but boiling range 100–140°C

obtain the quantitative results. The petroleum spirit 80/110 C contained 2·3 weight per cent benzene and 2·8 weight per cent toluene. The 100/140 C sample contained 0·6 weight per cent benzene, 5·4 weight per cent toluene, 1·3 weight per cent ethylbenzene, 2·5 weight per cent *m*- and *p*-xylene, and 1·0 weight per cent *o*-xylene.

This is a good example of the separation of different types of compounds which completely avoids the use of the FIA method to achieve the same separation. If the analysis of the paraffin portion had been required it could have been condensed from the gas stream and re-run under more suitable conditions.

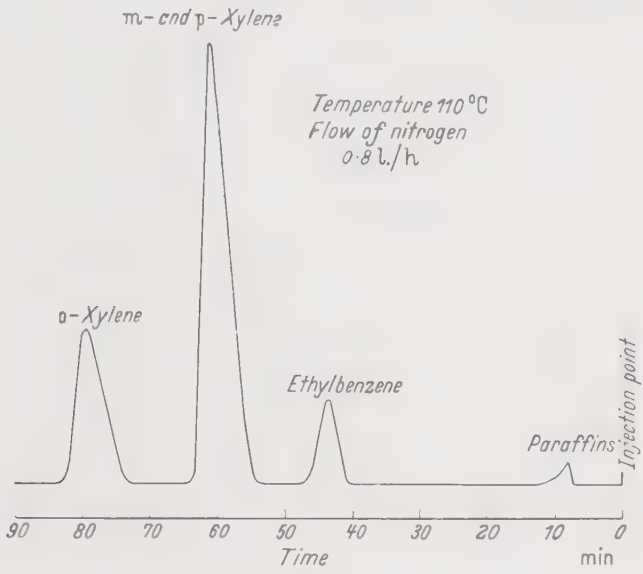

Figure 10. Analysis of industrial xylenes on fluorene picrate column

Industrial xylenes

The analysis of xylenes was satisfactorily accomplished on a fluorene picrate column. The paraffins present were separated as a group as noted above for the petroleum spirits. Generally, the total quantity of these has been determined separately by the FIA technique. Ethylbenzene and *o*-xylene are satisfactorily separated and determined by the area method. The trace of a typical sample containing 1·6 volume per cent paraffins, 10·8 volume per cent ethylbenzene, 58·3 volume per cent *m*- and *p*-xylene and 29·3 volume per cent *o*-xylene is shown in *Figure 10*. Trace impurities such as C_9 aromatics and toluene can be estimated by running at higher sensitivities. The sensitivity in *Figure 10* is about one quarter of that normally used.

Solvent mixture of oxygenated compounds

Fluorescent indicator adsorption analysis proved that the sample was essentially free from hydrocarbons and the elemental analysis indicated that the mixture consisted only of compounds containing carbon, hydrogen and oxygen. The constituents were identified on a DNP column and rechecked on a polyethylene glycol 400 column. The trace obtained on the DNP column is

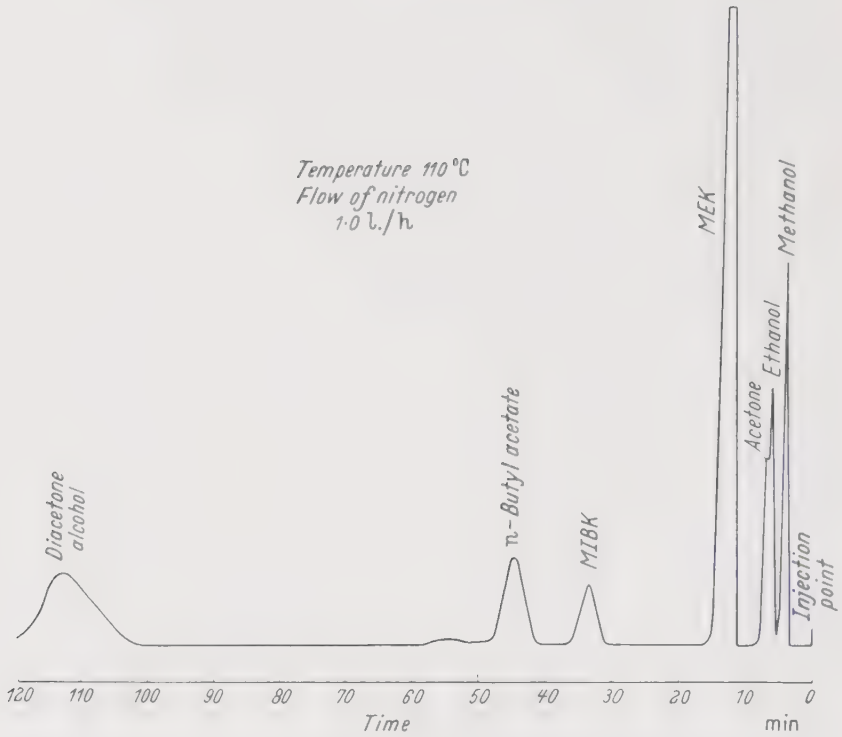

Figure 11. Solvent mixture of oxygenated compounds, using DNP column

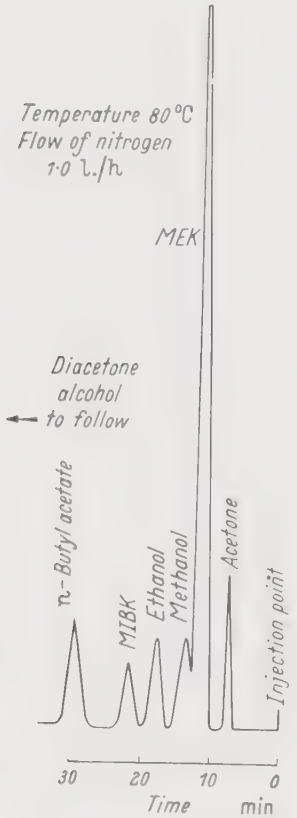

Figure 12. As Figure 11 but polyethylene glycol 400 column

shown in *Figure 11*. The determination of acetone and ethanol was carried out on the polyethylene glycol column, since these constituents were insufficiently separated on the DNP column. The trace is shown in *Figure 12*. Quantitative results were obtained by the addition to sample technique. The actual composition was methanol 12 volume per cent, ethanol 8 volume per cent, DAA 22 volume per cent, acetone 3 volume per cent, MEK 45 volume per cent, MIBK 4 volume per cent, *n*-butyl acetate 6 volume per cent, and a trace of water.

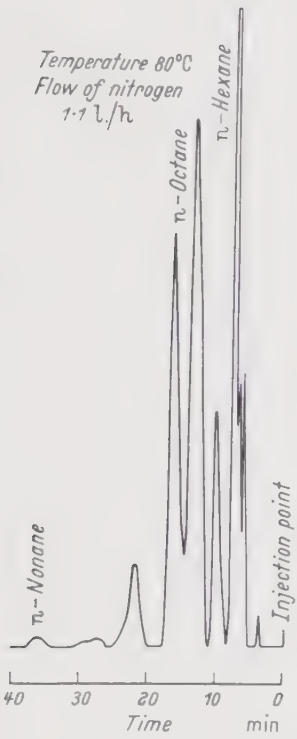

Figure 13. Analysis of paraffin portion from complex solvent mixture on DNP column

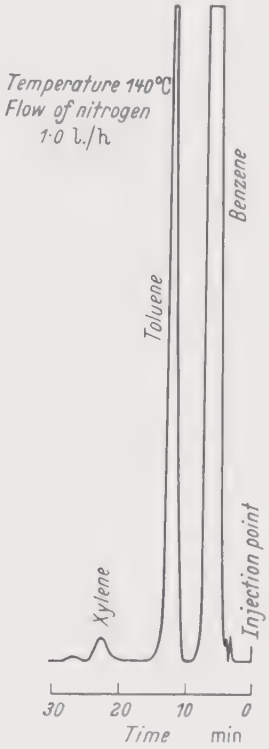

Figure 14. Aromatics trace from complex solventmixture on DNP column

Complex solvent mixtures

A typical complex solvent mixture consists of hydrocarbons blended with alcohols, ketones, and other oxygenated compounds. With a completely unknown sample the procedure already outlined is carried out, i.e. (*1*) routine tests, (*2*) type separation and determination, (*3*) identification and determination of constituent compounds. The composition of a complex solvent mixture is given in *Table I*. The paraffin portion of this solvent, separated by the FIA method, was analysed on a DNP column and the trace is shown in *Figure 13*. From this it was evident that a petroleum distillate boiling in the range 65–95 C was involved. The individual paraffins were not determined. The trace for the aromatic portion is shown in *Figure 14*. Most of the oxygenated compounds were identified by running on paraffin and polyethylene

Table I. Composition of a Complex Solvent Mixture as Determined with the Aid of GLPC

Constituent	Vol. per cent	*Constituent*	Vol. per cent
Petroleum spirit	16	*Tech. amyl alcohol*	17
Benzene	13	*Mesityl oxide*	1
Toluene	2	*DAA*	18
Acetone	10	n-*Butanol*	1
MEK	5	*Other minor constituents*	3
IPA	14	(*water, esters, etc.*)	

glycol columns (see *Figures 15* and *16*). Quantitative results were obtained by the addition technique. The C_5 alcohols were identified by condensing the relevant constituents from the GLPC gas stream and running on the mass spectrometer. The oxygenated compound fraction collected from the FIA

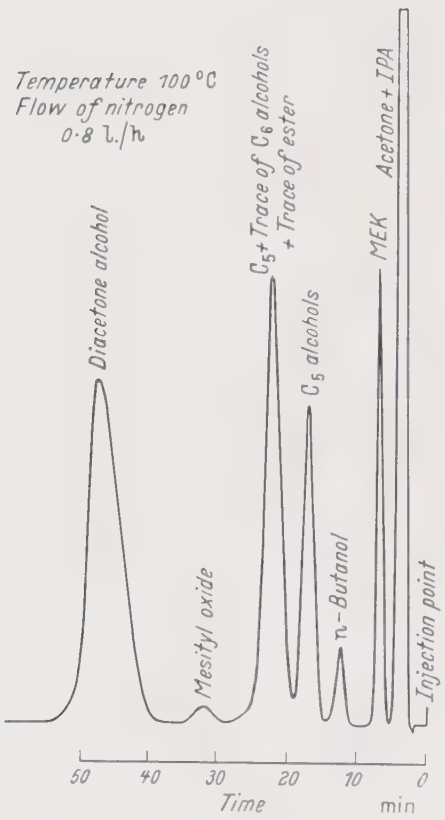

Figure 15. Oxygenated compounds from complex solvent mixture determined on paraffin column

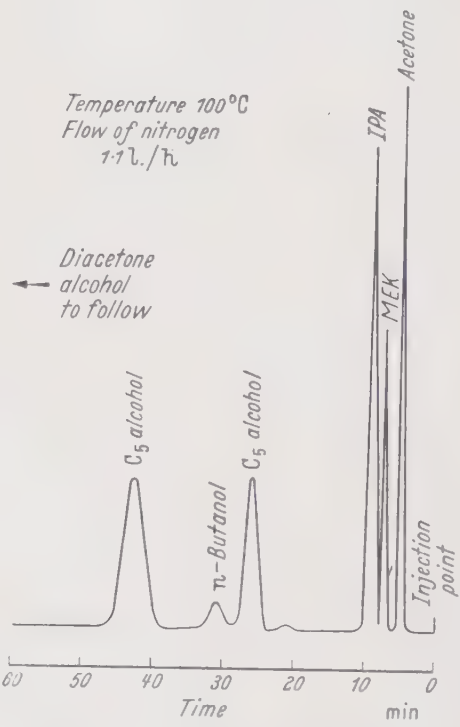

Figure 16. As Figure 15 but using polyethylene glycol 400 column

separation was not representative and it was necessary to apply a correction to the final analytical results for loss of acetone, MEK and C_5 alcohol, which apparently were partially by-passed by the butylamine displacer.

Aqueous solvents

The types of stationary phase which can be used satisfactorily with aqueous solvents are limited. Stationary phases which have a low water solubility, e.g. DNP and paraffin, are unsuitable for samples containing even small quantities of water. The water rapidly passes through columns packed with such liquids and there is a considerable tailing effect which upsets resolution and quantitative determination of constituents appearing later in the chromatogram. However, with stationary phases in which water is reasonably

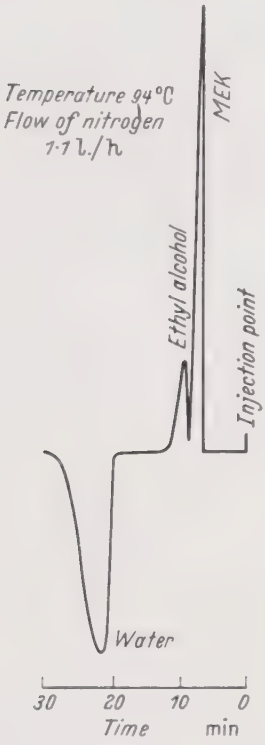

Figure 17. Trace of typical aqueous solvent mixture using polyethylene glycol 600 column

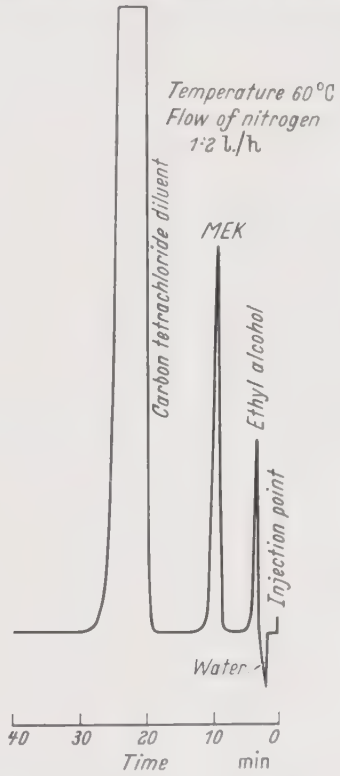

Figure 18. Trace of typical aqueous solvent mixture after drying, on paraffin column

soluble the tailing effect is largely absent and the water peak is displaced along the chromatogram to an extent depending on the degree of solubility. Polyethylene glycols have been found satisfactory for analysing aqueous solvents. The traces of a typical aqueous solvent containing 48 volume per cent MEK, 31 volume per cent ethanol and 21 volume per cent water are shown in *Figures 17* and *18*. Most of the water was removed from the sample run on the paraffin column by diluting with carbon tetrachloride and saturating with potassium carbonate according to the method of Ray[9]. It will be seen that the relative positions of MEK and ethanol have been completely reversed on the two stationary phases. On the polyethylene glycol column the compounds are in the reverse order of their boiling points owing to the greater relative solubility of the ethanol in this liquid. Quantitative results were obtained by the addition technique.

Abbreviations

DAA —Diacetone alcohol
DNP —Dinonyl phthalate
FIA —Fluorescent indicator adsorption
GLPC —Gas–liquid partition chromatography
IMS —Industrial methylated spirit
IPA —*iso*Propyl alcohol
MEK —Methylethyl ketone
MIBK —Methyl*iso*butyl ketone

The author wishes to thank the Directors of 'Shell' Research Limited for permission to publish this paper, also those members of the Thornton staff, particularly Mr E. R. Adlard, Mr J. A. K. Lawson and Mr P. J. Moore, who have taken part in the work described.

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DISCUSSION

G. F. Oldham: On page 400, Mr Whitham gives maximum temperatures for various stationary phases. I would be interested to know why he quotes outlet pressures. For some time I have been given the impression that many workers are ascribing incorrect reasons for the effects obtained by using low outlet pressures. On previous occasions I have inquired and the replies have been that by reducing the outlet pressure, high boiling solutes are volatile at lower temperatures, vapours enter the katharometer at lower pressures; here, stationary phases are implied to have different vapour pressures and recently it was implied that distillation under reduced pressure takes place in the column.

There are two distinct evaporative processes which might take place in a column. If the temperature is below the boiling point for a given pressure the liquid will exert its vapour pressure at that temperature independently of the permanent gas pressure (for a solute fraction in the stationary phase, Raoult's law or some deviation from it will apply). Distillation will only occur if this pressure is equal to or greater than the carrier gas pressure. Here the pure vapour will spread from the boiling liquid. If this took place in a column, no carrier gas would leave the column, only 100 per cent solute or stationary phase vapour. This of course does not occur in gas chromatography where about 4 per cent vapour is the highest concentration normally encountered.

The rate of loss of stationary phase from a column is proportional to the vapour pressure at the column temperature, corrected to 0 C, multiplied by the molecular weight and the volume gas flow measured at the exit temperature and pressure.

I feel it would have been of more significance to have quoted the vapour pressures at the maximum temperatures and the rates of flow employed.

D. GALL: At the Fuel Research Station we have been working on very similar lines to Mr Whitham's and can compare the value of the combination of fluorescent indicator adsorption and vapour-phase partition chromatography. A major interest of the Fuel Research Station is the investigation of the production of oils and chemicals from coal by the Fischer Tropsch catalytic synthesis from carbon monoxide and hydrogen. The main products obtained are water and a range of saturated and unsaturated hydrocarbons extending from methane to waxes containing about 100 carbon atoms per molecule. Although the hydrocarbons are predominantly aliphatic, naphthenic and aromatic hydrocarbons are present, together with oxygenated compounds such as alcohols, aldehydes, ketones, esters and fatty acids. The oxygenated compounds of low molecular weight are recovered in solution in the reaction water.

For analysis of the oil phase the technique used has been almost identical with that described by Mr Whitham, involving distillation, separations of the distilled fractions by FIA analysis and further analysis of the classes obtained by vapour-phase partition chromatography. For analysis of the paraffin and aromatic fractions, dinonyl phthalate and medicinal paraffins have proved satisfactory as stationary phases. For the oxygenated derivatives boiling below 150 C promising results have been obtained using cetyl alcohol. Celite 545 has been used as support, nitrogen as carrier gas and detection has been by katharometer.

The aqueous phase of the product contains approximately 10 per cent of organic material of which about half consists of fatty acids. A preliminary separation by ion exchange gives aqueous solutions of the acids and of the non-acidic material. Analysis of the latter is being carried out by vapour phase chromatography using columns of glycerol as suggested by Harvey and Chalkley followed by the nonyl phthalates or cetyl alcohol in series.

The main interest in this work lies in a study of the effect of the synthesis conditions (temperature, pressure, gas composition, etc.) on the nature of the products. It has been confirmed, following a limited series of analyses of the hexane fractions by infra-red spectroscopy, that the production of branched-chain paraffins relative to *n*-paraffins increases with increase in reaction temperature. The ratio of branched- to straight-chain compounds has been generally considered to be characteristic of the synthesis catalyst. Quantitative data of this kind which can only be obtained readily by vapour phase chromatography should throw considerable light on the mechanism of the Fischer–Tropsch and similar reactions.

R. L. BLACKMORE: I should very much like to ask the author what sort of effect he gets when he loads a half inch column with as much as 3 c.c. of a liquid. Admittedly he is only after a type resolution there, but I would be very glad if he would give a rough curve of the kind of separation he gets under those heavily loaded conditions.

B. T. WHITHAM: I would like to say a few words about the operation of columns under a vacuum. The main object, as far as we can see, of operating columns under a vacuum is to get increased sensitivity. You do increase the concentration of the constituent in the gas stream at the end of the column and consequently you do get a bigger response. We have recently been doing some work with high molecular weight substances and we have tried to keep the katharometer at as low a temperature as possible. It appears at the present time that if one operates the katharometer at low pressure one can keep the temperature down further than at high pressures. Now this evidently is very difficult to explain theoretically, but we have in actual fact experienced that one can take the pressure down and keep the temperature down whereas at high pressures you do get condensation effects in the katharometer. I am not quite sure whether the last speaker was talking about the fluorescent indicator adsorption method or GLPC.

R. L. Blackmore: My point is that if you put, say, 10 mg on a quarter inch tube you then put fifty times as much on a tube whose area is only four times as much. What sort of results have you got under the comparatively high loading?

B. T. Whitham: We have a considerably greater length as well, 27 ft as against 6 ft for our small columns. The loading which you put on this big column really depends on what you are trying to do. The degree of separation which you can achieve with sample sizes of 0·1 0·5 ml I should say in general is much higher than on the small 6 ft columns. But of course as one increases the sample size the degree of separation is naturally reduced due to the increasing band widths. As a guide I can only quote the example given in the paper. A 2 ml sample of *o*- and *p*-xylene can be completely separated in under four hours on a silicone 550 stationary phase at 100°C. These two hydrocarbons boil only 5C° apart.

J. Clifford: In connection with xylene analysis, on page 405 you will see Dr Whitham's analysis of a xylene mixture. It is possible to make this the basis of an extremely good method for the complete analysis of xylene mixtures, because the ordinary methods of infra-red spectroscopy are rather difficult when you have a large number of components. If you separate the *m*- and *p*-xylene peaks you can make a very accurate infra-red analysis of that. A combination of vapour phase chromatography and infra-red analysis gives a better method of xylene analysis than any other I can think of. Quite apart from that what we have been trying to do is to find a method of xylene analysis which can be used in a laboratory not possessing infra-red equipment. We made use of the fact that the optical absorption of *p*-xylene at 266 μ is twice that of *m*-xylene. Consequently a mixture of the two can be analysed easily with a simple absorption instrument, which all laboratories possess nowadays. This is done either by separating out the components and doing the analysis then, but it is easier and for most practical purposes it is sufficient, if you want an analysis, say, within 3 or 4 per cent, to do the ultra-violet absorption on the mixture as a whole and simply run the chromatogram. By this method we do quite accurate complete analyses of xylene mixtures which would be quite difficult otherwise.

G. F. Oldham: The point Mr Whitham has made that by using low exit pressures it is possible to use a katharometer at lower temperatures may possibly be explained if there is a narrow jet at the end of the column across which there is a sudden pressure drop. In this case the bulk of carrier gas would expand and the solute vapour, no longer being in equilibrium with the liquid phase, would also expand to give a lower partial pressure.

As regards large samples on columns, the effect depends on the nature of the mixture. I have added as much as 600 μl to a 6 mm diameter column of 4 ft length using a hydrogen flame detector. The sample consisted mainly of ethanol and carbon tetrachloride in unknown proportion together with 0·01–0·04 per cent concentrations of higher alcohols. The early part of the chromatogram consisted of an extremely large mixed peak of ethanol and carbon tetrachloride, followed by the higher alcohols with surprisingly little widening of the bands.

It was asked earlier if it were possible to measure accurately an early peak of large height but very narrow width. If all the fractions are separated by at least one minute of base line this is possible by adding the sample slowly over the course of one minute. All the bands will be widened to the extent of one minute, but retaining their original areas. The early peak will be many times wider and lower and easy to measure accurately whereas later peaks will only be wider and lower by a small percentage. There is the further advantage that one is using a more linear range of the detector. As the tall early peaks will now be much lower it is often possible to use a larger sample and thus obtain greater accuracy also on small late peaks.

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THE USE OF GAS–LIQUID CHROMATOGRAPHY IN THE DETERMINATION OF THE DISTRIBUTION OF AROMATIC COMPOUNDS IN COAL TAR NAPHTHAS

D. W. Grant and G. A. Vaughan
Coal Tar Research Association

The problem of separating paraffins from aromatic compounds of similar boiling points and also of determining the important compounds indene and coumarone have been largely overcome by the use of tricresyl phosphate as a stationary phase in the analysis of coal tar naphthas. Theoretical considerations were applied to find the efficiency of a column which would separate the major components sufficiently to eliminate mutual interference at the peak maxima. Examples from a survey of fourteen tar assay naphthas are given together with a complete table of results.

The majority of coal tars contain between one and three per cent of neutral compounds which distil between the xylenes and naphthalenes. These compounds constitute the naphtha fraction of coal tar and this is important industrially as a solvent and as a source of indene–coumarone resins.

The distribution of components in this range varies considerably according to the temperature and type of coal carbonization but is usually of a complex nature. For this reason little progress had been made in the analysis of coal tar naphthas until the advent of gas–liquid chromatography. This technique was admirably suited to the problem owing to the promise it gave of rapid and complete analyses.

This paper describes part of the work undertaken at the Coal Tar Research Association in which attention was restricted to components boiling between 150°C and 183°C.

Apparatus

The chromatographic apparatus used for the investigation was of a standard type employing the thermal conductivity method of detection. The column was electrically heated and the detector cells were maintained at room temperature. In the analysis of high boiling components, the detector cell attached to the column outlet was maintained at a reduced pressure in order to avoid condensation.

Partition columns were U-shaped for the sake of compactness and were fitted with a three-way tap for the introduction of samples. Samples were

'injected' on to the column by means of a small glass pipette which could be inserted through the three-way tap and so into a heated zone.

Experimental

Samples of coal tar naphthas which had been produced during the assaying of coal tars were considered as suitable subjects for the investigation. These were produced by fractional distillation of neutral oil and consisted of the fraction boiling between 150°C/760 mm and 137°C/100 mm of mercury. Fourteen such naphthas were obtained and of these four were from vertical retort tars, two from horizontal retort tars, six from coke oven tars and two from tars produced by low temperature processes. Paraffin contents of the naphthas were determined by adsorption chromatography on silica gel and showed considerable variation. In general, coke oven naphthas were very low in paraffin concentration but others were rich in paraffins, especially the low temperature naphthas.

Initial experiments showed that the major problem in the analysis would be the separation of paraffins from aromatic compounds of similar boiling points. Preliminary separation by adsorption chromatography was not possible since a quantitative recovery of the aromatic constituents could not be obtained. It was necessary, therefore, to find a stationary phase which would decrease the retention volumes of paraffinic compounds so as to avoid their interference with the aromatic compounds.

Four stationary phases were evaluated by chromatographing a mixture of aromatic hydrocarbons and a mixture of straight chain aliphatic hydrocarbons on four columns of similar dimensions. The columns were maintained at 100°C with a nitrogen flow rate of 30 ml/min.

Retention volumes for all the peaks were calculated in units of the benzene retention volume. Results are given in *Table I*.

It is evident that while the nature of the stationary phase has little effect on the relative positions of the aromatic hydrocarbons, the paraffins are affected considerably. On tricresyl phosphate, for instance, normal decane, b. pt 174°C, emerges from the column well before ethylbenzene, b. pt 136°C, its retention volume being about a quarter of the value obtained on liquid paraffin. Coal tar naphthas contain paraffins which have nine or ten carbon atoms per molecule and so by using tricresyl phosphate in columns designed to analyse these materials, the paraffins should emerge from the column as a separate group of peaks, preceding the main aromatic portion of the naphtha. A typical example is reproduced in *Figure 1*. The naphtha is from a vertical retort source and was chromatographed on a 10 ft long column operated at 130°C.

Separation of Aromatic Components in Naphthas

Owing to the complexity of the aromatic components of coal tar naphthas and the proximity of many of their boiling points, columns of normal length, viz. 5 to 6 feet, were not sufficient for the separation in quantitative analysis. Complete separation of the peaks was impracticable and in any case unnecessary where analysis is carried out by peak height measurement, and so it was desired to construct a column which would separate the components just sufficiently to eliminate mutual interference at the peak maxima. Simple

Table I. Effect of Stationary Phase on Relative Retention Volumes of Aromatic and Aliphatic Hydrocarbons

Stationary phase	*Aromatic hydrocarbons*				
	Benzene	*Toluene*	*Ethyl-benzene*	m-*Xylene*	o-*Xylene*
Liquid paraffin	1	1·99	4·54	5·17	6·08
Silicone fluid M.S. 550	1	2·00	3·92	3·92	4·85
Dinonyl phthalate	1	2·23	4·36	4·86	5·90
Tricresyl phosphate	1	2·05	4·08	4·27	5·32

Stationary phase	*Aliphatic hydrocarbons*			
	n-*Hexane*	n-*Heptane*	n-*Octane*	n-*Decane*
Liquid paraffin	0·673	1·36	2·91	12·73
Silicone fluid M.S. 550	0·462	0·800	1·56	6·07
Dinonyl phthalate	0·369	0·811	1·61	6·84
Tricresyl phosphate	0·246	0·443	0·820	3·28

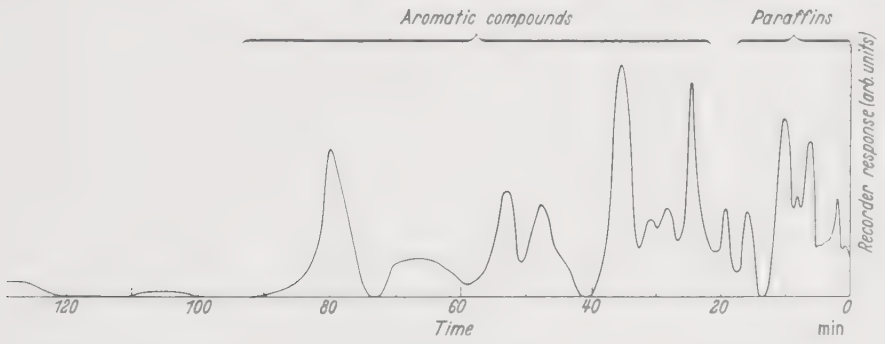

Figure 1. Gas–liquid chromatogram of vertical retort naphtha showing the effect of tricresyl phosphate on paraffinic components

T = 130°C. *Nitrogen flow rate* = 25 ml/min. *Inlet pressure* 1060 mm, *outlet pressure* 700 mm *of mercury*

theoretical considerations were applied to find the approximate column efficiency which was required, as follows.

It can be shown[1] that the approximate efficiency of a column which is required in order to separate two close boiling aromatic hydrocarbons by $2x$ standard deviations is given by the expression

$$r = 0{\cdot}0298x^2T^2/d^2$$

where T = temperature of column in °K, d = difference between the boiling points of the two compounds.

For quantitative analysis by peak height measurements, the peaks must be separated by at least three standard deviations, i.e.

$$x = 1{\cdot}5 \quad \text{and} \quad r = 0{\cdot}067T^2/d^2$$

For the column to be suitable for application to coal tar naphthas it should be capable of separating components with a boiling point difference of 2° C. Hence, at a column operating temperature of 130° C, an efficiency of at least 2700 theoretical plates is required.

Experience has shown that on the average, the HETP of a gas–liquid column is about 1 mm and so by constructing a column with a length of 270 cm, the required efficiency should be realized.

A column was constructed from four lengths of glass tubing so as to give an overall length of 300 cm with an internal diameter of $\frac{1}{4}$ inch. The tubes were packed with a mixture of graded Celite 545 and tricresyl phosphate in the ratio 10 : 3 by weight. The sections were joined together laterally by means of small glass capillary U-tubes which were fixed firmly into the wider tubes by means of silicone rubber tubing. In this way the column occupied the same space in the column heating jacket as a column having half the length and bent into a single U shape. The efficiency of the column was determined at 130° C from measurements on the peak widths due to a simple mixture[2]. The efficiency was 2600 plates and so the column was considered to be suitable for the analysis.

Identification and Analysis

During the course of earlier work it was noted that values of

$$\log \frac{\text{Retention volume of aromatic compound}}{\text{Retention volume of benzene}}$$

varied linearly with the boiling points of the aromatic compounds in a restricted boiling range. Graphs of this nature were therefore prepared by chromatographing a synthetic mixture of aromatic compounds on two columns, one containing dinonyl phthalate and the other, tricresyl phosphate as stationary phases. In this way, certain compounds were observed to behave in a specific manner. Thus, while 'inactive' hydrocarbons, such as the trimethyl benzenes, showed little variation on altering the stationary phase, compounds which contained an olefinic grouping were retarded more on tricresyl phosphate than on dinonyl phthalate. Hydrindene, also, was retarded on the former stationary phase. It is probably fortuitous that, whereas no separation occurs between hemimellitene, hydrindene and coumarone on a dinonyl phthalate stationary phase, separation of all three compounds is easily accomplished on a column containing tricresyl phosphate. These effects can be seen clearly in *Figure 2*. The behaviour of paraffins, which has been described previously, is also apparent.

By observing the behaviour of peaks from the chromatography of the coal tar naphthas on the two columns, and relating them to *Figure 2*, identification of all the major constituents boiling up to indene was easily carried out. Final confirmation was made in each case by adding pure substances to the naphthas and chromatographing them.

Quantitative analysis was carried out on the fourteen tar assay naphthas using the internal standard technique. *cyclo*Hexane was used as an internal

standard and calibration factors were obtained by chromatographing pure samples made up into synthetic mixtures. Calibration factors, i.e.

$$\frac{\text{Peak height due to component}}{\text{Concentration of component}} \cdot \text{Peak height due to constant concentration of } \textit{cyclo}\text{hexane}$$

were independent of concentration under constant operating conditions and provided that the column capacity was not exceeded. It was at first feared that this may not apply with indene and coumarone owing to the ease with which

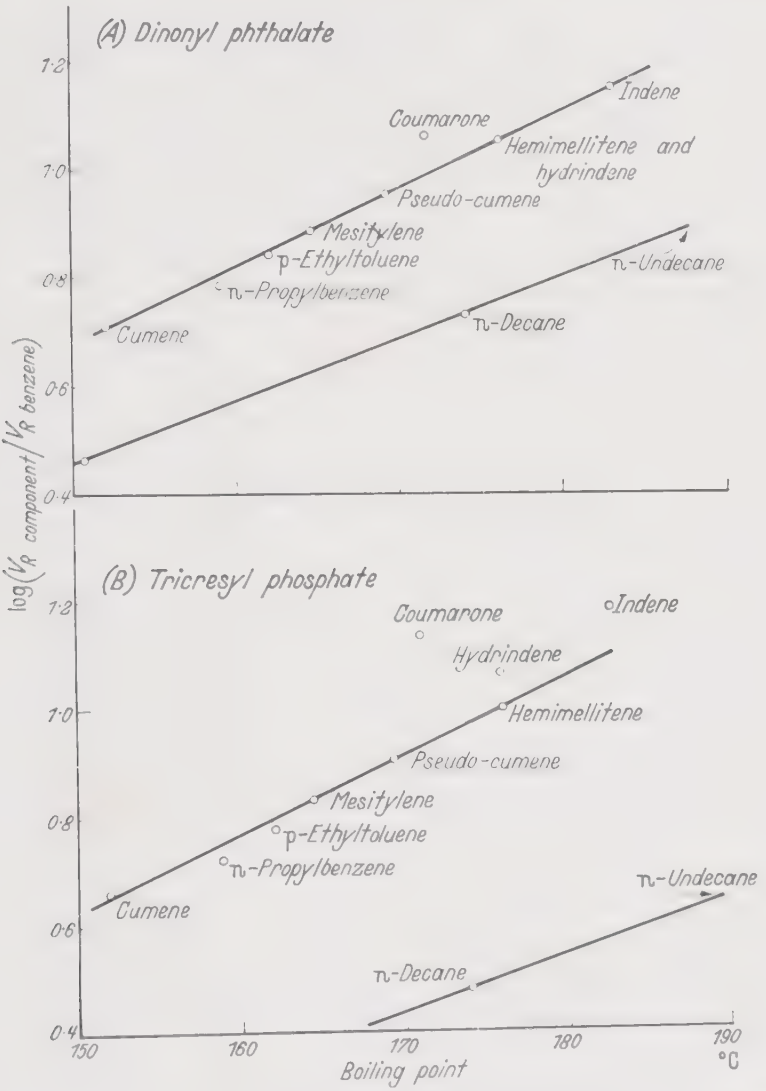

Figure 2. Relationship between boiling point and retention volumes for naphtha constituents on two stationary phases

they polymerize in adsorption chromatography. The factors for these compounds, however, were also constant and showed that no polymerization occurred in the gas–liquid partition column.

Some examples of chromatograms which were obtained during the analysis of coal tar assay naphthas are given in *Figure 3*.

Full analytical results for the fourteen naphthas are given in *Table II*.

Review

Each chromatogram produced during the analysis was found to be characteristic of the naphtha to which it was due, and little similarity existed between them. Certain broad distinctions were apparent, however, according to the source of the naphthas. Those derived from coke ovens were generally of a simple nature and contained high concentrations of hydrindene and indene.

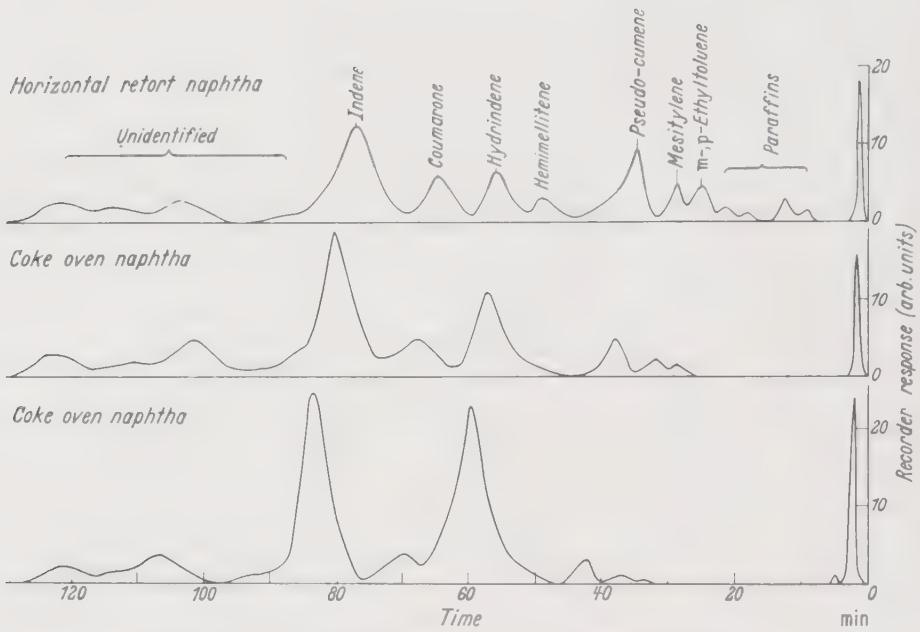

Figure 3. Chromatograms of coal tar assay naphthas

Column temp. = 130°C. *Column*—300 cm, *tricresyl phosphate. Inlet pressure*—1060 mm *of mercury. Outlet pressure*—700 mm *of mercury. Nitrogen flow rate*—25 ml/min

This is no doubt due to the tendency for cyclization to occur under the conditions which exist in coke ovens, and this view is justified by the lower values for alkyl benzenes.

Horizontal and vertical retort naphthas, on the other hand, contain a more even distribution of the aromatic materials and a higher concentration of benzene homologues which possess ethyl or propyl groups. Unfortunately the paraffin shift was not sufficient to prevent interference with the *n*-propylbenzene peak and so the data given for this compound cannot be considered as reliable.

The two low-temperature naphthas gave very complex chromatograms due to the high proportion of paraffinic compounds which are present. Considerable interference was experienced on many of the peaks from *cyclo*paraffins which are not removed to the same extent as open chain paraffins. For this reason the values which are given for these naphthas must be regarded as tentative.

Table II. Summary of Results Expressed as % w/w of Component in Naphtha

Type of naphtha / *Component*	*1* V.R.	*2* V.R.	*3* V.R.	*4* V.R.	*5* H.R.	*6* H.R.	*7* C.O.	*8* C.O.	*9* C.O.	*10* C.O.	*11* C.O.	*12* C.O.	*13* L.T.	*14* L.T.
n-*Propylbenzene*	*Interference from paraffins*		2·4	*Interference from paraffins*		1·1	—	—	2·2	—	—	—	7·0	*Interference* 6·0
m-, p-*Ethyltoluenes*	5·1	5·2	3·7	3·5	2·4	2·4	0·5	0·3	1·9	1·8	3·8	0·7	4·0	
Mesitylene	2·7	2·8	1·7	1·9	0·8	2·8	0·7	0·6	1·8	3·8	3·0	1·0	2·7	3·7
Methylstyrene	1·8	1·9	1·3	1·2	—	*Trace*	—	—	—	—	—	—	2·1	3·0
Pseudo-cumene	5·9	7·5	4·7	7·5	5·6	6·8	4·7	2·1	4·4	9·5	5·4	3·1	7·3	9·8
Unidentified	2·8	1·2	1·4	1·0	2·0	2·4	—	—	—	—	—	—	3·4	3·5
Hemimellitene	4·1	4·3	9·5	2·8	2·0	3·0	2·3	2·6	*Trace*	4·4	*Trace*	1·5	8·1	7·3
Hydrindene	7·7	5·9	3·8	4·6	7·7	9·7	6·5	22·6	17·5	29·9	11·6	14·7	10·5	7·3
Coumarone	3·1	1·6	2·0	2·2	7·1	8·2	4·9	3·5	7·4	8·2	7·2	6·2	6·0	3·0
Unidentified	3·0	1·5	*Trace*	*Trace*	—	—	—	—	—	—	—	—	*Trace*	*Trace*
Indene	17·5	11·1	9·7	13·9	1·9	24·4	26·5	35·1	21·5	6·3	11·2	33·0	*Interference*	
Paraffins	14·8	24·0	9·5	23·7	4·5	5·5	5·2	*Trace*	1·2	0·3	3·1	2·0	28·0	33·4
Total	68·5	67·0	49·7	62·3	34·0	66·3	51·3	66·8	57·8	64·2	45·3	62·2	79·1	77·0

V R.—Vertical retort. H.R.—Horizontal retort. C.O.—Coke oven. L.T.—Low temperature.

Obviously, a considerable amount of work remains to be done in this field. It is hoped that in the near future gas liquid chromatography will enable us to identify the components of naphthas which occur beyond indene in the distillation range and also to estimate them quantitatively. The presence of high paraffin concentrations, which include *cyclo*paraffins, has been shown to have deleterious effects on the separation and this is one of several remaining problems which must yet be solved.

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DISCUSSION

Editor's Note: During the presentation of his paper Mr Grant described a new detector he had developed, which employed a microflame similar to that described by Mr Scott and others but the luminosity of the flame rather than its temperature was measured. He mentioned that the exit hydrogen from the column was carburetted and also that the detector produced a very much larger response for aromatic than for saturated hydrocarbons.

R. P. W. Scott: I have had the opportunity of seeing Mr Grant's detector in operation, and it worked extremely well. I believe an important factor is the carburation of the exit gas with benzene before burning in the detector. This gives a certain base luminosity to the flame which gives it a linear relationship with the mass. The application of this detector could be very wide, particularly in measuring the quantity of aromatics. I think it might possibly be extended to the identification of aromatics and paraffins in the high boiling range by the type of response. It seems worth while to try and combine this emissivity detector and the normal flame detector.

A. Klinkenberg: I have been struck by the great simplicity and practical form of the equation

$$Z = 0{\cdot}0298\, x^2T^2/d^2$$

expressing the required number of stages (Z) in terms of degree of separation (as distance between peaks), boiling temperature T and boiling temperature difference d.

Another approach for a similar purpose is Glueckauf's well known graph. In a few words I would compare the two. Glueckauf refers to separation in terms of peak areas, the present treatment to peak heights. Glueckauf deals with neighbouring components present in widely different ratio, the present treatment does not. The present formula, on the other hand, is extremely simple. It may therefore be useful to consider the scope of the equation and its limitations. If one assumes validity of Trouton's law where

$$\text{heat of vaporization/absolute boiling point} = C$$

the constant in Mr Grant's equation should be $4R^2/C^2$. This limits the treatment to non-associated fluids. Expressed in cal(C)$^{-1}$ mole^{-1} $R = 2$ and $C = 22$ which gives 0·033, a value close to the one given. It is valid for atmospheric pressure.

On the one hand the applicability of this equation is therefore wider than indicated, namely only aromatic hydrocarbons, but on the other hand there has been assumed equality of activity coefficients, i.e. ideality or identical deviations from ideality. Judging from *Figure 2* of the paper, the non-benzenoid aromatics do not fit in this picture. I should like to ask the authors whether the constant given has also been derived from Trouton's law or is an empirical one.

D. W. GRANT: I would like to reply to Dr Klinkenberg that the constant in this equation was indeed derived from Trouton's law and is specifically applied here to aromatic hydrocarbons.

A. KLINKENBERG: You have probably taken a higher value for the constant than I have.

D. W. GRANT: I think we took 23 in that.

A. KLINKENBERG: Perhaps then the 298 has one decimal too much. Trouton's law is not as accurate as that, I believe.

D. W. GRANT: Of course we do fully realize that.

G. J. MINKOFF: I would like to make a very quick suggestion for combining the two burners, on the assumption that you are measuring the radiation emitted, which is, of course, mostly in infra-red and comes mainly from hot carbon dioxide and hot water molecules. Normally when there is nothing coming out you are measuring radiation from the steam. When you get organic vapours coming through you get radiation from the carbon dioxide which is considerably more intense. This may not, however, be the mechanism.

G. A. P. TUEY: I should like to suggest another way of combining Mr Scott's hydrogen flame with the photoelectric detector. Why not allow the flame to impinge on a suitable grid, such as a piece of a Welsbach gas mantle, whose luminosity is a function of flame temperature? This would avoid the problem of uniform carburation to maintain a steady luminosity in the flame.

W. A. WISEMAN: It seems to me the great thing about this particular detector is its selectivity and any method of eliminating this seems to me to be a step in the wrong direction.

35

GAS CHROMATOGRAPHIC SEPARATION OF HYDROGEN ISOTOPES

E. GLUECKAUF and G. P. KITT
Atomic Energy Research Establishment, Harwell

Complete purification of deuterium from deuterium–hydrogen mixtures has been achieved by passage of a 1 : 1 mixture through a column containing palladium black on asbestos, at room temperature. A column containing 20 g of palladium can deal with approximately 1 litre, s.t.p., of mixture.

GAS chromatographic separation of isotopes has previously been attempted by us with the neon isotopes[1], but the differences in their adsorption coefficients on charcoal are so small that only enrichment and not complete separation was achieved.

The differences in the adsorption coefficients of the various hydrogen isotopes (hydrogen, deuterium, tritium), however, are larger than those of many vapours which can be separated by gas chromatography and a separation in charcoal columns is quite feasible. But hydrogen is a diatomic gas, and a separation of, say, a hydrogen–deuterium mixture would give three fractions H_2, HD and D_2. This is a considerable inconvenience for two reasons. First, the separated HD has to be recycled after treatment with a catalyst which produces more of the pure molecular 'species'. Secondly, the separation factor between any two species in the sequence is on the average only half as big as between the extremes, with the result that the separation becomes more difficult, the columns longer and the overlap of the adjoining bands greater. This situation can be remedied by the use of an adsorbent that simultaneously catalyses the conversion of HD into $D_2 + H_2$. Such a material is palladium black, where the hydrogen is interstitially 'dissolved' in atomic form.

The adsorption of hydrogen and deuterium has been studied by Sieverts and Danz[2], by Gillespie and Downs[3], and by others, and it was known that deuterium is considerably less strongly adsorbed than hydrogen. As the result of the dissociation of the gas molecule on adsorption, one obtains at low pressures an adsorption isotherm of the general shape[2]

$$\theta \propto p^{1/2}$$

This, in view of its exponential nature, results in chromatographic elution bands having extreme 'tailing' properties, which are quite unsuitable for resolution into isolated bands[4]. It was clear, therefore, that under these conditions, the method of displacement chromatography[5] would have to be applied. As we are interested in the total separation and recovery of the less

adsorbed deuterium only, it was possible to use pure hydrogen as a displacing agent. Regeneration of the column could be carried out (*a*) by evacuation of the heated column, (*b*) by following this up by an oxidizing treatment with air, to remove any last traces of hydrogen.

Experimental

(a) *Single stage experiments*

Batch equilibrations were carried out between a given amount of adsorbent and a given volume of gas space. The D/H ratios before and after equilibration

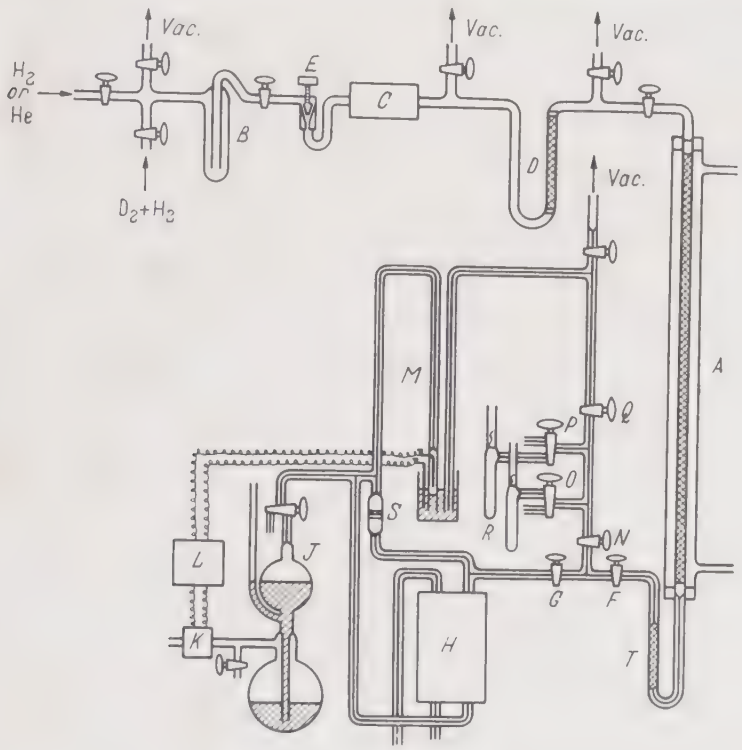

Figure 1. Apparatus for chromatographic separation of hydrogen isotopes

were determined mass-spectrographically and from the data the single stage separation factors were obtained.

(b) *Column experiments*

1. *Apparatus—Figure 1* shows diagrammatically the apparatus used in the experiments with palladium–asbestos columns.

Deuterium gas was prepared by passing heavy water steam of high purity (99·7 per cent or better) over coarse iron filings held at 600–800 C. The water from the equilibrium mixture so obtained was removed with a cooled trap and the deuterium was passed into a calibrated storage vessel sealed with vacuum oil. Samples of gas of varying composition were obtained by adding quantities of hydrogen to the deuterium in the calibrated vessel. Equilibrium between H_2, HD and D_2 was obtained immediately on entering the palladium column.

The column (*A*), containing 20 g of palladium black mixed with 6 g of purified asbestos, was 44 cm long and of 0·8 cm internal diameter. It was initially packed closely but without undue pressure, in order to avoid excessively slow flow rates. On evacuation of the column, the packing usually tended to break at the top but on readmitting gas to the column, the palladium–asbestos mixture could be resettled by gentle tapping. The column was jacketed and could be maintained at different temperatures by passing suitable coolants.

Gases were fed into the column at constant pressures up to 24 cm of mercury above atmospheric pressure through the liquid nitrogen cooled trap (*B*), the flowmeter (*C*), and the short column (*D*), 10 cm long and of 0·6 cm internal diameter, filled with 2 g of 40–60 mesh activated gas charcoal for purification from heavier gases. The needle valve (*E*) permitted a control of the gas flow rate.

From the bottom of the column, the gases passed through a short tube (*T*), containing 1 g of 'anhydrone' and then through taps (*F*, *G*) into the katharometer (*H*). The katharometer was by-passed by a lute (*S*), across which a small pressure drop was maintained, by which means the maximum flow rate through the katharometer was fixed. The katharometer, kindly loaned by I.C.I. Ltd, consisted of an aluminium block containing two identical cells, having identical wire filaments. Through one cell gas from the column was passed whilst the other served as a compensating resistance in a simple Wheatstone bridge network. By maintaining a constant bridge current and fixed sensitivity for the galvanometer, the relative katharometer response to the passage of purified hydrogen, deuterium and helium was found to remain constant.

From the katharometer, gas could be either passed to waste or into the calibrated mercury-sealed storage vessel (*J*). The pressure was maintained constant as the vessel filled by the controlled release of air pressure through the electromagnetic valve (*K*) which was operated with the relay (*L*) in conjunction with a contact at the bottom of the manometer (*M*). Through taps (*N*, *O* and *P*) samples of gas could be taken into sample tubes (*R*) for subsequent examination by mass spectroscopy.

2. *Pre-treatment of column*—At the completion of each run, the column was normally regenerated in the following way. The hydrogen was pumped off from the whole apparatus and the temperature of the column raised to 100°C. The evacuated apparatus was then isolated from the pumping manifold and slowly filled with dried air, the temperature of the column still being maintained at 100°C. The air was pumped away and the gas charcoal (*D*) activated by heating with a yellow gas flame. The appropriate cooling fluid was circulated through the column jacket, the gas charcoal column immersed in liquid nitrogen and the column slowly filled with helium as the buffering gas.

3. *Experimental methods*—Column experiments of the following types were carried out:

(*i*) Simple break-through experiments in which mixtures of H_2, HD and D_2 were passed into the column, displacing the helium buffering gas, until the feed composition appeared in the effluent.

(*ii*) Displacement experiments in which limited amounts of mixtures of

varying composition were adsorbed on the column and then displaced by a stream of pure hydrogen.

Subsequently, it was found unnecessary to fill the column with helium since equally satisfactory separations were obtained by slowly passing the gases into the evacuated column, the gas eventually collecting at the bottom of the column being found to be of similar purity to that when a helium-filled column was used.

The air treatment of the column which was carried out to remove any strongly adsorbed residual hydrogen always resulted in the production of a small quantity of heavy water, which preceded the deuterium band, and which

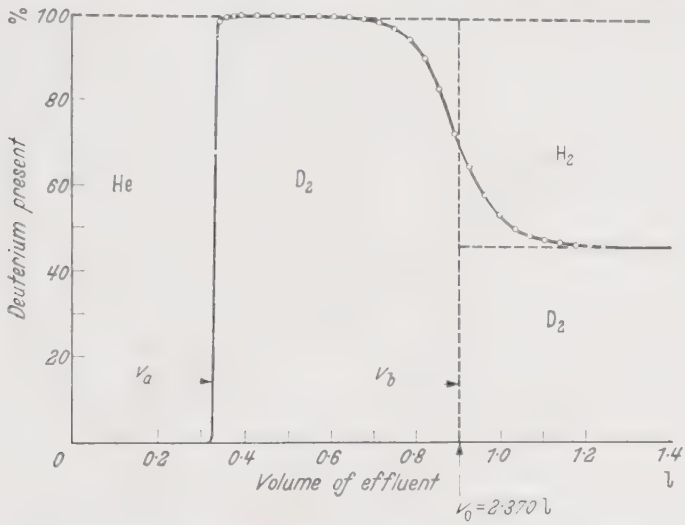

Figure 2. Break-through elution curve of hydrogen–deuterium mixture from palladium column. Approximate flow rate 2·5 litres per hour

could be collected as product, if necessary. But it was found later that the column operated quite satisfactorily without air treatment, the gas separated having the same order of purity as that separated from an air-treated column.

It must be stated, however, that the purity of gas samples separated was determined by a mass-spectrographic method and the accuracy of measurement of high purity samples on the machine used is open to conjecture. It may be that air treatment of the column is essential for obtaining a high purity product, but it would also be necessary to work with a metal apparatus and take special precautions to avoid chemical exchange between the separated product and the adsorbed water vapour on the walls of the receiving end of the column and the storage vessel.

Determination of separation factors by the break-through technique. In view of the small gas samples, single stage equilibrations did not give very accurate results, and the separation factor was therefore determined also by the break-through technique.

Here, a mixture of hydrogen and deuterium was fed into the column filled with helium, until first pure deuterium and later the original mixture broke through in the effluent. The volumes of both the inflowing and outflowing gases were determined. Looking at the elution curve (see *Figure 2*), we can define the volumes v_a and v_b by the lines which intersect the elution boundaries

in such a way as to produce equal areas on either side. At the effluent volume v_b, we have the feed volume v_0 of the hydrogen–deuterium mixture. Then we can state two equations of mass conservation:

Total feed of hydrogen $(v_0 \cdot c_H)$ = amount of hydrogen adsorbed $(X \cdot f_H + Y \cdot c_H)$ + amount of hydrogen eluted

and similarly for deuterium.

The hydrogen equation then leads to

$$v_0 \cdot c_H = (X \cdot f_H + Y \cdot c_H)$$

The deuterium equation gives

$$v_0 \cdot c_D = (X \cdot f_D + Y \cdot c_D) + (v_b - v_a)c'_D$$

where c_H, c_D are the gas concentrations in mole/litre of the inflowing gas, c'_D that of the outflowing gas, which can be derived from the knowledge of

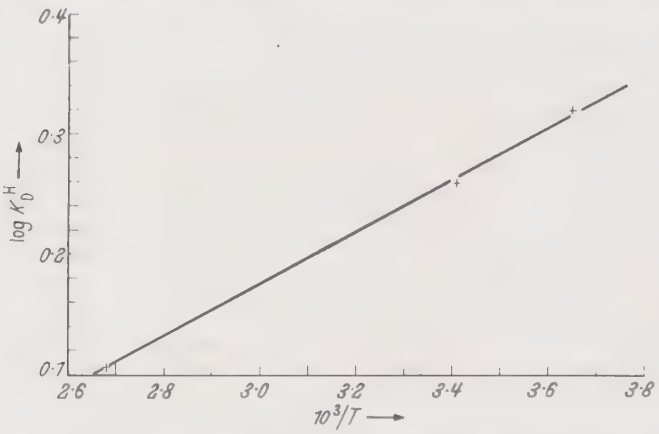

Figure 3. Temperature dependence of deuterium–hydrogen separation factor.
+ Break-through experiments
○ Mass-spectrographic analyses of single stage equilibrations

partial pressures and temperatures. f_H and f_D are the amounts adsorbed in equilibrium with the feed gas, per volume unit of column. X is the number of volumes (ml) of column. Y is the dead-space of the apparatus from the feed point to the analyser. It is obtained experimentally by the displaced volume of helium,

i.e. $$Y = v_a$$

Eliminating X from the two equations we obtain for the separation factor K_D^H

$$\frac{1}{K} = \frac{c_H}{c_D} \cdot \frac{f_D}{f_H} = 1 - \frac{(v_b - v_a)c'_D}{(v_0 - v_a)c_D} = 1 - \frac{(v_b - v_a)P'}{(v_0 - v_a)x_D \cdot P}$$

where the P's are pressures, and x_D the mole fraction of deuterium in the feed. The results are shown in *Figure 3* for the different temperatures and can be represented by the equation

$$\log K_D^H = 215/T - 0{\cdot}47$$

between 0 and 100 C. The temperature coefficient is similar to that observed by Gillespie and Downs, but not the absolute value.

Separation of pure deuterium by displacement gas-chromatography. The break-through technique, though producing pure deuterium, does not utilize the mixture completely but leaves the column saturated with a mixture of hydrogen and deuterium. A complete utilization can be obtained by using pure hydrogen as a displacing gas. If the displacement boundary were quite sharp, it would be possible to load the column to an extent given by $(K - 1)/K$, but in view of the diffuseness of the boundary, better results are being obtained with a somewhat smaller loading. *Figure 4* shows the elution

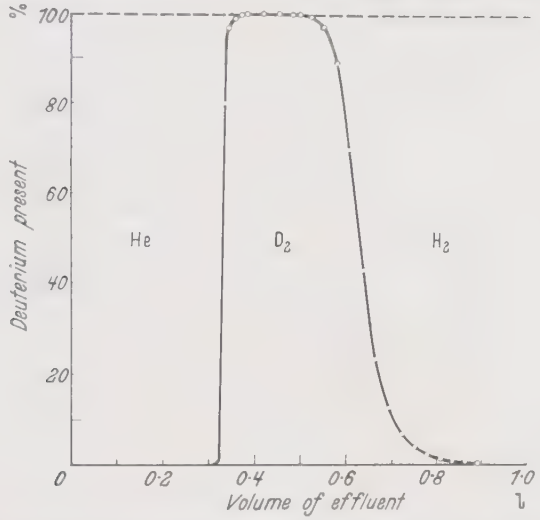

Figure 4. Elution curve of a chromatographic separation by displacement. Original mixture 47 per cent *deuterium. Flow rate* 2·5 litres per hour

diagram of such a separation using a loading of 40 per cent of the column capacity with a mixture $H_2 : D_2 \simeq 1 : 1$. As the column length was adequate for separating the load, no mixed band appeared in the eluate, apart from the short overlap zone, resulting from the interdiffusion of the two gases.

The main value of the gas chromatographic separation of hydrogen and deuterium lies in the possibility to produce deuterium of unprecedented purity from hydrogen–deuterium mixtures. It is not expected to be of importance in the production of deuterium from mixtures of natural abundance, not only on account of the discontinuous operation of chromatographic columns but also because of the great quantities of palladium required for the retention of the vastly more abundant hydrogen. Experiments to produce super-pure deuterium are continuing and it is hoped to give the results at the meeting.

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Note: Discussion relating to Chapter 35 appears at the head of page 432.

36

THE QUANTITATIVE SEPARATION OF MIXTURES CONTAINING VINYL ACETATE AND BROMOTRICHLOROMETHANE BY VAPOUR PHASE CHROMATOGRAPHY

J. C. Robb and D. Vofsi
Department of Chemistry, The University, Birmingham

A method of achieving a good quantitative analysis of mixtures containing vinyl acetate and bromotrichloromethane is described in which the method of vapour phase chromatography is used to separate the constituents of the mixture which are then frozen out from the exit gas stream in a trap and weighed. The quantities of material used are of the order of 500 mg. The recovery is quantitative to within about 1·5 mg or less. This method, where applicable, removes the necessity for carrying out calibration experiments such as are necessary when peak areas are measured.

In a kinetic study of the addition of bromotrichloromethane (BTM) to vinyl acetate (VA) in the region of high VA/BTM ratios, the need arose for a quantitative simultaneous determination of both reactants. The reaction is photochemically initiated and a trichloromethyl radical is produced as in reaction (1).

$$BrCCl_3 + h\nu \rightarrow Br^{\bullet} + {}^{\bullet}CCl_3 \quad \ldots.(1)$$

$${}^{\bullet}CCl_3 + CH_3COOCH{=}CH_2 \rightarrow CH_3COO\dot{C}H{-}CH_2CCl_3 \quad \ldots.(2)$$

$$CH_3COO\dot{C}H{-}CH_2CCl_3 + BrCCl_3 \rightarrow CH_3COOCH(Br)CH_2CCl_3 + {}^{\bullet}CCl_3 \quad \ldots.(3)$$

$$R + CH_3COOCH{=}CH_2 \rightarrow \text{polymer of vinyl acetate} \quad \ldots.(4)$$

This $^{\bullet}CCl_3$ radical then adds to a molecule of VA as in reaction (2) and the adduct radical R then abstracts a bromine atom from a molecule of $BrCCl_3$ as in reaction (3). It will be seen that reactions (2) and (3) constitute a chain process which produces the 1 : 1 adduct of BTM and VA. However, at low concentrations of BTM, an additional reaction becomes possible, namely that shown in reaction (4) where an adduct radical R can add to another VA molecule so increasing the molecular weight of the radical and leading to formation of polyvinyl acetate. The point of major interest in this investigation is that by varying the amount of BTM it should be possible to grow radicals of a desired size so that the reactivities of these radicals in reactions (3) and (4) can be measured as a function of their size. For simplicity in the above reaction scheme, the termination reactions of the chains have

been omitted. Since it is extremely difficult to handle the adduct and the polymer (both being very involatile and somewhat unstable), a quantitative determination of the constitution of the products of reaction is not possible by conventional distillation techniques. The relative occurrence of reactions (3) and (4) could, however, be estimated by following the rate of disappearance, due to reaction, of both VA and BTM. Such an estimation must be made for both constituents from each experiment.

The experimental conditions of interest are such that ratios of VA/BTM of the order of 10/1 to 40/1 must be employed. It is also necessary to allow only about 10 per cent of the lesser component to be removed in the course of reaction. This imposes rather strict accuracy requirements on the separation method to be used, and it seemed that vapour phase chromatography would have to be adopted. However, even in this case, the necessary accuracy could not be achieved in the conventional way by measuring peak areas since the calibration could become laborious. It was found that the quantitative recovery of the volatiles, separated by passing through a vapour phase chromatograph column, was sufficiently good to permit a high accuracy by trapping the individual components and weighing them. It was found convenient to work with samples of about 500 mg.

Apparatus and Procedure

The column *E* had an internal diameter of 10 mm and was surrounded by a vapour jacket, in which a constant temperature of 78°C was maintained by refluxing carbon tetrachloride. The total length of the column was 140 cm. At the top was connected a preheater tube *A* of 8 mm internal diameter, which was kept at 80°C by means of a heating coil. *D* is the sampler tube, having a B7 standard cone extended to a capillary tip at the bottom end. It is connected at the upper end by means of a rubber tube, *B*, to the nitrogen inlet tube as shown in *Figure 1*.

At the bottom end of the column a fine tungsten wire, *F*, having a resistance of about 130 ohms at 78°C was sealed in. This wire constituted one arm in a Wheatstone bridge and served as an indicator. As its counterpart, a simple radio resistance of about the same value was used in the bridge. The other components of the circuit were inexpensive radio types.

A Cambridge Instrument Co. galvanometer was used. It should be pointed out that, for the purpose of routine analysis of known components, once the time of their appearance and disappearance at the column outlet was established at fixed conditions of column operation, the indicator system could be dispensed with, so that the collecting traps could be switched in by indication of a clock.

The components of the mixture were collected in two traps having the dimensions indicated; they were filled with loose glass-wool in order to avoid entrainment. The traps were connected in series by means of B7 standard joints, which were ground in with fine carborundum, and finally with zinc oxide, in order to make as good a fit as possible. They were not greased.

The column was packed with kieselguhr, impregnated (to 45 per cent of its weight) with dinonyl phthalate.

To start an analysis, a weighed amount of about 500 mg of mixture was

introduced into the sampler tube *D*, and the tube sealed. After placing it in position, its upper tip was broken by a twist of the rubber tube, and the tube then turned round thus breaking its lower tip. Stopcock *C* was then closed, and the dry nitrogen stream, which was previously adjusted to 6 litres/hour, allowed to flush the sampler tube for 2 minutes. The stopcock was then re-opened.

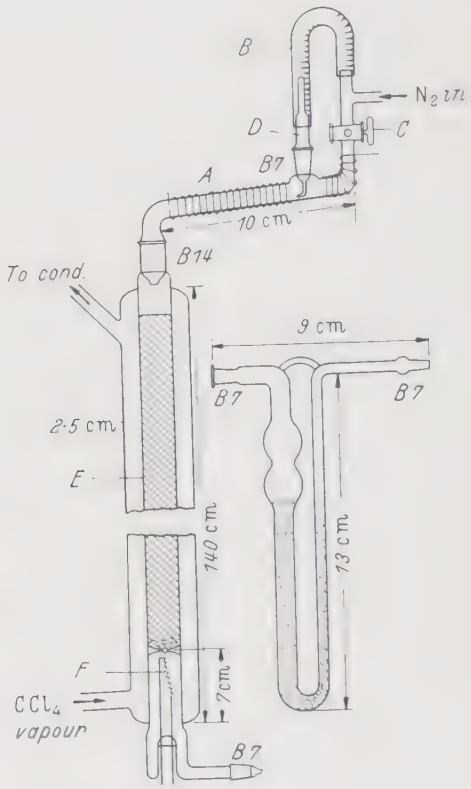

Figure 1. Arrangement of apparatus

Meanwhile, the second trap, in which the more volatile component (VA) was to be collected, was immersed in a liquid air container, so that the portion filled with glass-wool was just covered.

Under the stated conditions of nitrogen flow and column temperature, this component appeared at the column outlet 4·5 minutes after the introduction of the sample, and its flow was practically complete 5 minutes after its appearance. Another 7 minutes was allowed for collection of traces appearing in the form of a drawn-out tail before the first trap was submerged in liquid air. In this trap, BTM began to collect 22 minutes after zero time. 33 minutes after the introduction of the sample, both traps were quickly disconnected and closed with polythene plugs. The use of standard glass stoppers must be avoided, since after warming up, losses in these volatile substances occur owing to a slight build-up of pressure in the traps.

In order to avoid errors due to moisture condensation, a procedure of carefully wiping the traps with lens paper just before weighing was adopted. This was found more satisfactory than keeping the traps in a desiccator. Results are summarized in *Table I.*

Table I. Summary of Results

No.	*BTM in* mg	*BTM recovered* mg	*Δ* mg	Per cent *error*	*VA in* mg	*VA recovered* mg	*Δ* mg	Per cent *error*	*Adduct 1 : 1 retained* mg
1	66·0	66·2	+0·2	0·30	—	—	—	—	—
2	46·3	46·6	+0·3	0·65	—	—	—	—	—
3	23·9	24·0	+0·1	0·42	—	—	—	—	—
4	28·0	28·4	+0·4	1·40	—	—	—	—	—
5	28·5	29·7	+1·2	4·20	—	—	—	—	—
6	32·5	33·0	+0·5	1·60	—	—	—	—	—
1	—	—	—	—	496·5	496·5	—	—	—
2	—	—	—	—	505·1	503·7	−1·4	0·28	—
3	—	—	—	—	498·6	497·6	−1·0	0·20	—
4	—	—	—	—	493·5	491·4	−2·1	0·43	—
5	—	—	—	—	493·2	490·4	−2·8	0·57	—
6	—	—	—	—	510·4	508·6	−1·8	0·35	—
1	38·8	39·8	+1·0	2·6	507·8	507·9	+0·1	—	—
2	36·6	37·2	+0·6	1·6	478·8	477·8	−1·0	0·21	—
3	40·6	41·9	+1·3	3·2	531·8	532·5	+0·7	0·13	—
4	40·2	41·2	+1·0	2·5	526·6	526·4	−0·2	0·04	—
5	38·7	39·9	+1·2	3·1	506·9	506·9	—	—	—
6	42·5	43·9	+1·4	3·3	556·2	556·2	—	—	—
1	53·3	53·6	+0·3	0·56	436·0	435·4	−0·4	0·09	12·7
2	63·5	63·5	—	—	519·2	517·0	−2·2	0·43	15·1
3	51·9	51·1	−0·8	1·5	424·7	425·0	+0·3	0·07	12·3
4	50·0	51·2	+1·2	2·4	408·6	408·8	+0·2	—	11·9
5	57·3	56·2	−1·1	1·9	468·4	466·9	−1·5	0·32	13·6

Conclusion

The following remarks have to be made after examining the results of *Table I.*

(*1*) The absolute error is of the same order of magnitude for each of the components, although somewhat smaller for BTM. It very rarely exceeds 2·0 mg, and usually does not exceed 1·5 mg.

(*2*) The maximum relative error is therefore much greater for BTM (3 per cent) than for VA (0·5 per cent), since in our particular problem the latter component is present in excess.

(*3*) The data given in the table were obtained from analyses run in groups and it will be noted that, within each group, the errors seem to be in one direction. (This is particularly noticeable in the first three groups.)

The reason for this is now being investigated. Variations in column temperature and rate of flow are now being changed in order to obtain optimum conditions for the separation and recovery of the above components.

The authors are indebted to Professor H. W. Melville, F.R.S., for his interest in this work and one of them (D. V.) would like to thank Imperial Chemical Industries Ltd for the award of a Fellowship.

Questions were then invited on any point relating to Chapters 30–36.

A. J. P. MARTIN: I would like to ask Dr Glueckauf to what the value he gave for the separation factor related? Is the difference between the calculated and experimental values due to slowness of the interchange of the HD with H_2 and D_2?

E. GLUECKAUF: The separation factor which has been determined is one referring to the separation between the end products. Did I understand Dr Martin correctly in that he asked whether the difference between 2 cm and 1 cm is due to slowness of reaction?

A. J. P. MARTIN: Yes.

E. GLUECKAUF: Personally I would think that the difference between 2 cm and 1 cm in plate height is within the limits of estimated error.

A. F. WILLIAMS: Referring to the paper presented by Dr Vofsi I might say that we have used vapour phase chromatography to separate methylstyrenes and ethylbenzenes without any interference by polymerization. We started out with the idea of using an inhibitor on a column but found this was not essential.

Now as to the manner of behaviour of thermistors, which was discussed a little earlier I believe by Dr Minkoff, I have a few points which I wish to make. In picking thermistors you must take into consideration the fact that there are as many thermistors as there have been types of katharometer cells described at this meeting. The idea is to pick one you think will suit your need, and order a series of them and make certain that they fulfil the required conditions. In our particular case we were using 100,000 ohm units which are glass coated. We run them at 300 C for 100 hours. Out of that we get several thermistors which are quite well matched over a fairly large temperature range. I would like to point out that the most important factor determining the sensitivity is the slope of the resistance/temperature curve; compared with the slope of platinum or tungsten I think that the slope of thermistors is much greater even at 200 or 250 C. In higher temperature operation at 200 C, the thermistor itself is only 69 C higher, which I think is considerably lower than any katharometer where we are using tungsten or platinum. We have used our thermistor cell up to temperatures of 250 C over a matter of several months and found it quite reliable and stable.

W. A. WISEMAN: I often wonder why there has never been any mention of what one might describe as a cold wire katharometer, operated by heating the outer jacket and measuring the resistance of the inside wire with a very low current running through it. I was wondering if anybody had thought of this idea or done any work on it, or had any suggestions as to whether it would work. It seems to me it would eliminate the troubles people seem to be having with very hot wires in their katharometers.

J. G. AMESZ: In connection with Mr Hausdorff's paper, when he was discussing the features of chromatography, I was thinking about the Dutch proverb which says 'A good wine does not need recommendation'.

Secondly, the author was comparing those different techniques of ultraviolet, infra-red and mass spectrometry. I had the feeling that we should not do that. We have different techniques and they should not have to struggle for life against each other, but they should go hand in hand. We have had some examples this afternoon, for instance the xylene analysis. Moreover, some of the data given by Mr Hausdorff were not quite correct. If I am right *n*-butane and *iso*butane can be determined by mass spectrometry; *n*-butylene and *iso*butylene cannot, but they can be determined by infra-red. Also the seven components of C_4 gas mixtures can be determined easily quantitatively by infra-red. Furthermore I am very happy that I can tell some of our friends from abroad some more about Europe; that there is a small

country called Holland where some people still wear wooden shoes, but that there is a refinery of Shell's there where we do chromatographic analysis from plant streams coming from thermal catalytic crackers, solvent plants, even of compounds from insecticides, and so on.

Finally I am very happy that we have someone here from the technical side, who takes the trouble from our shoulders in manufacturing apparatus. I have seen the Perkin Elmer instrument working, and I saw they use straight columns. This morning we talked about straight tubes and spiral tubes, so I would like to put a question to Mr Hausdorff. Has his firm done something about this subject and have they found some features about straight tubes instead of the spiral rounded ones?

N. H. Ray: I would also like to ask Mr Hausdorff a question, if I may do so. Could he tell us what column packing he used, and what was the stationary phase?

H. H. Hausdorff: The stationary phase used on those twelve hydrocarbons was tri*iso*butylene at room temperature at about 30 per cent concentration with Celite sieved to approximately 100–150 mesh.

About the columns, I do not think that you could call them straight tubes because they are actually bent in the form of a W about 50 cm high, i.e. 2 m total column length. This is easy for filling. The tube is filled when it just has one U bend, then it is bent again afterwards which is a simple operation.

I am sorry I have raised a national issue here between Europe and the U.S.A. For your information I would like to point out that I am European myself but I have been given the opportunity of spending half my life over there and half my life here. I have gained the impression, not that people were doing more quantitative work over there than here, but that the majority of people who were involved in this field in the U.S.A. had more interest in the quantitative aspects than in the qualitative. Whether this is an advantage or disadvantage is immaterial.

R. H. Powell: It seems to me that if a technique is to be widely adopted the apparatus needed should be readily available. Not all workers can make their own apparatus. I speak, of course, as one particularly interested in the manufacture and the sale of apparatus, but who also must provide workers with the type of equipment which they need. A manufacturer has to incur considerable cost before he can go into production.

When the subject is new many fertile minds throw up ideas in profusion, and we have had during these last three days sufficient to think about certainly for some little time to come. There are dozens of ideas now that are worthy of closer attention. Not all of them, of course, will survive. The manufacturer who enters the market early takes a certain commercial risk in doing so, because when the subject is young and has aroused the interest which VPC has aroused, the rate of progress is exceedingly rapid. The manufacturer of the equipment, therefore, who holds back a bit and waits until the dust of controversy has settled, may well find that the subject has been sufficiently clarified for the different views of workers to be in some degree reconciled and for the design considerations therefore to be made rather clearer.

I feel now that the Organizing Committee of this Symposium deserve the very warmest possible tribute for their enterprise. I think they have done exceedingly well. They have put up a subject which is new, and the attendance of you all is an eloquent tribute to their work. But I feel they might be able to do still more for the advance of VPC by defining the characteristics that ideally they would seek to embody in the equipment which you yourselves may use in the future. The variables in VPC are now fairly well known, but opinions on the value of those variables is by no means uniform. The characteristics of a good detector have been defined in principle by Dr James, and I am glad to know that we have had some discussion on thermistors. Helical columns versus W-shaped or straight columns have aroused a great deal of interest and a great deal of difference of opinion. There are no settled

views, as I understand the discussion, on the merits of positive pressure versus vacuum pumps. People talk about steady rates of flow. I have not heard any definition this afternoon of what constitutes a steady rate of flow; what tolerances should be placed upon the temperature control of the column itself. We have workers who work with vapour jacket columns; we have workers who work with electrically heated chambers, all these things are of great interest to the manufacturer of equipment who wants to be able to supply workers with what they want, but first, of course, he wants the workers to define the conditions they want the apparatus to fulfil. These conditions clearly depend on the use made of the apparatus. In this country price is very often much more important than it is elsewhere. New workers have to be trained, possibly in technical colleges. These colleges are themselves impecunious and will not pay £500 or £600 for apparatus. They want a piece of equipment for which they can get an educational grant of £200. What can we, the manufacturers, do for £200?

These to me, as an apparatus manufacturer, are very important considerations. I have heard people here say that the apparatus ought to be made for £135. Many people in this country make their own equipment. Of those people who do, I wonder how many really know how much it costs them. I have heard people in the U.K. evaluate the cost of a research worker in the large organizations as £2 10*s*. an hour. Similarly, the amount given for the cost to a large American organization, including overheads, is $15.42 an hour. Now the comparable value of that at the current rate of exchange is about £6 an hour. So these things want really equating, and if somebody who is working in the VPC field and desires to construct his own apparatus really knew how much it cost him to make, he might consider that the apparatus made by a man whose job it is to make apparatus might not, in the end, be more expensive than it apparently is if made in his own laboratory. So a buyer really gets what he pays for. A manufacturer can provide anything that is required if the buyer will pay for it. The technical colleges and universities very often will not.

So I feel that the Organizing Committee, while they are very much to be congratulated on the success of this Symposium, may well be doing still more for the more rapid and widespread adoption of vapour phase chromatographic methods by giving some consideration to defining the variables, and the precision with which those variables ought to be controlled and measured, for the apparatus manufacturer who will make the apparatus which he hopes they may ultimately buy.

CLOSING ADDRESS

B. W. Bradford

This Symposium has been looked forward to for some time. As some of you know, we had hoped to hold it last year, but owing to various circumstances that was not possible. On one or two occasions I have been a little late at this series of meetings and I have found the house full and have had to stand at the back. I rather feel that if we had postponed the meeting any longer we should have had to hire the Albert Hall to hold all the people who wanted to attend. There were about 400 registrations, which is a very large number for a specialized conference. That, I think, is the only proof which is necessary of the need for it and of its popularity. Vapour phase chromatography is expanding so fast that this meeting has been able to deal with a wide range of development which has occurred in a remarkably short space of time. It cannot have happened very often in a meeting of this sort that one could have present so many of the people who have taken an active part in its development and whose names must appear in every well regulated list of references. It would be invidious to mention all their names but I think you would wish me to make an exception in the case of Dr Martin who did so much to start this powerful new technique and, as has been said by several speakers, who had done so much to help and inspire many who have worked in the field. I think we owe him a great debt in this matter.

I have heard most of the papers and discussions, and it has been quite fascinating right the way through, at any rate to me. It has been both interesting and lively: in spite of the frequent reference to flames, however, it has never been really heated and in spite of the many references to coiled columns it has never really got twisted up very badly. I think it has been a very good conference, and I think we have had most of the aspects of the subject very well discussed, both inside and outside the meetings.

What is the outcome going to be? We—by which I mean the Hydrocarbon Research Group of the Institute of Petroleum—organize these conferences on various techniques from time to time, so that as many workers as possible both inside and outside the petroleum industry can benefit by exchange of views and experience. Moreover, physical techniques are usually of greatest use in the study of hydrocarbons and it happens that the petroleum industry is often first in the field in its interest in them. That is the main reason for our having sponsored this meeting. Of further developments, I can only say at the moment that this is a matter under discussion, but I think it is very likely that we shall form a chromatographic panel of the Hydrocarbon Research Group and that we shall develop our specialized interest in it in this way. I have no doubt that later on the standardization aspect, which has been referred to on a number of occasions at this meeting, will be taken up more seriously: I have no doubt that the statisticians will move in, and that such hopeful estimates of accuracy as 1 per cent of the amount present will start to fall by

the wayside. This meeting has certainly given a powerful impetus to chromatography and I am sure that we shall carry on from it and use the impetus to stimulate still further the scientific basis of the study of chromatography, of which the foundations have been so excellently laid in the working committee's recommendations which we have just heard from Dr Martin. Although the hydrocarbon interest is only a fraction of the enormously wide field of chromatography I hope—just as a personal opinion—that we shall not have too many chromatographic groups and societies formed, as has happened in certain other techniques.

I now want to refer to some personalities to whom we owe this excellent conference. It is quite obvious to everybody that it has required a lot of organizing and a great deal of hard work. I have been told by the Chairman of the Organizing Committee, Dr Birch, that I must not mention his name so I will refrain from doing so, but I must mention Mr Rampton because he keeps everybody in such a good temper all the time. All the contributors and many others have cause to appreciate Mr Desty's kind but firm efficiency and I must say to him how much everybody appreciates his editorial efforts. I must also tell you that he was called away suddenly in the midst of the arrangements and Mr Harbourn had to deputize for him, and we must thank Mr Harbourn as well as Mr Desty for what was done. I do not know whether it is a record to have a bound volume of preprints ready weeks before the date of the meeting, but it is certainly very rare, and that has helped enormously, for which the organizers and the publishers are to be thanked.

Finally, the international aspect of this meeting has been one of its most pleasing features. We have had representatives from most parts of the world. There is a strong contingent from Holland, all of whom have been very stimulating; I think we are all pleased to see them moving in with their characteristic efficiency on to the subject of chromatography. From other countries in Europe, as you know, we have also had some excellent contributions, and some very notable ones from the U.S.A. and Canada. To all our guests we say how happy we are to have had them here, and finally I hope we shall have another such occasion before very long.

The Conference concluded

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